

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-331088

(43)Date of publication of application : 14.12.1993

(51)Int.Cl.

C07C 39/16  
B01J 23/04  
B01J 31/10  
C07C 37/84  
// C07B 61/00

(21)Application number : 04-316351

(71)Applicant : CHIYODA CORP

(22)Date of filing : 30.10.1992

(72)Inventor : SHINDO AKIO  
SAKASHITA KOJI  
YASUI MAKOTO  
ASAOKA SACHIO

(30)Priority

Priority number : 03311991    Priority date : 30.10.1991    Priority country : JP

(54) PRODUCTION OF BISPHENOL A AND TREATMENT OF MOTHER LIQUID SEPARATED FROM CRYSTALLIZATION PRODUCT OF PHENOL SOLUTION CONTAINING BISPHENOL A

(57)Abstract:

PURPOSE: To provide the method for producing bisphenol A efficiently preventing the accumulation of by-products and impurities in the reaction system and obtaining the highly pure bisphenol A as a crystal adduct with phenol.

CONSTITUTION: The method for producing the bisphenol A by reacting acetone with an excessive amount of phenol in the presence of an acid catalyst comprises (i) a distillation process comprising feeding at least one of the circulated mother liquid into a distillation tower and subsequently distilling off 50-90wt.% of the mother liquid fed into the distillation tower to obtain the distillate containing phenol, (ii) a heating process comprising heating the bottom liquid of the distillation tower obtained in the process (i) in the presence of a basic catalyst at 200-350° C, (iii) a vacuum-recovering process for vacuum-distilling the product obtained in the process (ii) to obtain a distilled vapor containing the phenol and isopropenylphenol, (iv) a rapidly cooling process for bringing the distilled vapor obtained in the process (iii) into contact with the distillate obtained in the process (i) to rapidly cool the distilled vapor, and (v) a circulation process for circulating the rapidly cooled product obtained in the process (v) to the reaction process.

## LEGAL STATUS

[Date of request for examination] 01.08.1996

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]	2796557
[Date of registration]	03.07.1998
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

Copyright (C); 1998,2003 Japan Patent Office

## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## CLAIMS

---

### [Claim(s)]

[Claim 1] The resultant acquired from the reaction process which makes an acetone and the phenol of an excessive amount react under existence of an acid catalyst, and makes bisphenol A generate, and this reaction process An acetone, The separation process divided into water, a phenol, and the phenol solution containing bisphenol A, The crystallizing process which deposits the crystal adduct of bisphenol A and a phenol from the phenol solution containing this bisphenol A, In the manufacture approach of bisphenol A which consists of a circulation process which circulates the mother liquor obtained at the crystallization product separation process and this crystallization product separation process of separating crystal adduct and a mother liquor from the crystallization product obtained with this crystallizing process to said reaction process (i) The distillation process which obtains the distillate which is made to distill 50 – 90% of the weight of the mother liquor which introduced these some circulation mother liquors [ at least ] into the distilling column, and was introduced into this distilling column, and contains a phenol, (ii) Reduced pressure evaporation of the product obtained at the heating process which heats the bottom of the distilling column obtained with this distillation process (i) at 200–350 degrees C under existence of a basic catalyst, and this (iii) heating process (ii) is carried out. The reduced pressure recovery process of obtaining the distillate steam containing a phenol and an isopropenyl phenol, (iv) The manufacture approach of bisphenol A characterized by including the quenching process which the distillate steam obtained at this reduced pressure recovery process (iii) is contacted to the distillate obtained with the distillation process (i), and quenches it, and the circulation process which circulates through the quenching object obtained at (v) this quenching process (iv) at a reaction process.

[Claim 2] The approach of claim 1 which performs a heating process (ii) and a reduced pressure recovery process (iii) to coincidence using a reactor.

[Claim 3] The approach of claim 2 which circulates to a reactor after heat-treating a part of the bottom at the temperature of 200–350 degrees C under existence of an extract and a basic catalyst from a reactor.

[Claim 4] One approach of claims 1–3 of circulating at a reaction process, after facing circulating through the quenching object obtained at the quenching process (v) at a reaction process and contacting this quenching object on strong acid mold ion exchange resin.

[Claim 5] It faces processing the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A. (i) The recovery process which obtains the distillate which is made to distill 50 – 90% of the weight of the mother liquor which introduced these some mother liquors [ at least ] into the distilling column, and was introduced into this distilling column, and contains a phenol, (ii) Reduced pressure evaporation of the product obtained at the heating process which heats the bottom of the distilling column obtained with this distillation process (i) at 200–350 degrees C under existence of a basic catalyst, and this (iii) heating process (ii) is carried out. The vacuum distillation process which obtains the distillate steam containing a phenol and an isopropenyl phenol, (iv) Art of the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A characterized by including the quenching process which the distillate steam obtained at this reduced pressure recovery process (iii) is

contacted to the distillate obtained with the distillation process (i), and quenches it.

[Claim 6] The approach of claim 5 which performs a heating process (ii) and a reduced pressure recovery process (iii) to coincidence using a reactor.

[Claim 7] The approach of claim 6 which circulates to a reactor after heat-treating a part of the \*\*\*\*\* at the temperature of 200-350 degrees C under existence of an extract and a basic catalyst from a reactor.

---

[Translation done.]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the art of the mother liquor separated from the crystallization product of the phenol solution containing the manufacture approach of bisphenol A, and bisphenol A.

[0002]

[Description of the Prior Art] In order to manufacture bisphenol A [2 and 2-screw (4'-hydroxyphenyl) propane], the thing [ bottom / of existence of an acid catalyst ] which you react and is made for an acetone to react to a superfluous phenol is known. Moreover, in order to carry out separation recovery of high grade bisphenol A from this resultant, crystallization of the resultant is carried out, the crystal adduct (only henceforth crystal adduct) of bisphenol A and a phenol is deposited, and removing a phenol from the obtained crystal adduct is also known (JP,36-23335,B, JP,52-42790,B). Furthermore, carrying out the cyclic use of waste water of the mother liquor (phenol solution) after separating the crystal adduct obtained with said crystallizing process to a reaction process is also known.

[0003] by the way, to the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A 2-(2'-hydroxyphenyl)-2 which is the isomer of little bisphenol A besides a lot of phenols and bisphenol A -(4'-hydroxyphenyl)- Propane (It is only hereafter called 2 and 4'-bisphenol A) etc. -- by-products, such as a bisphenol compound, a tris phenol, a polyphenol compound of the amount of macromolecules, and a chroman compound, -- containing -- further -- \*\*\*\* -- a small amount of coloring impurity and the coloring nature impurity are contained. And since this mother liquor contains that colored impurity and impurity which is easy to color, it serves as a colored liquid which gives high coloring concentration with heating. Although the reuse of it is circulated through and carried out to the system of reaction since such a mother liquor contains bisphenol A which is the phenol and the specified substance used as the reaction raw material of bisphenol A, when it circulates as it is, since are recording of said by-product, and a coloring impurity and a coloring nature impurity takes place, it is necessary to perform removal of those by-products and impurities. For this reason, it faces carrying out the cyclic use of waste water of the mother liquor to the system of reaction, some mother liquors [ at least ] are contacted to the adsorbent which consists of acid type cation exchange resin, and the approach (JP,55-34779,B) of carrying out adsorption treatment of the coloring object, and circulating through it to the system of reaction after that is learned. However, by this approach, since adsorption treatment of some impurities in a mother liquor is only carried out, in a circulation mother liquor, the by-product or impurity of a considerable amount cannot still remain, and that are recording cannot be prevented.

[0004] According to JP,1-230538,A, the resultant which a phenol and an acetone are made to react and is acquired is carried out the 1st \*\*\*\*. A series of primary routing which obtains the 1st crystal adduct and the 1st mother liquor from the obtained 1st crystallization product, removes a phenol from the 1st crystal adduct and obtains bisphenol A, The resultant which mixes an isopropenyl phenol and a phenol to said 1st mother liquor, is made to react under existence of an acid catalyst, and is acquired is carried out the 2nd \*\*\*\*. The 2nd crystal adduct

and the 2nd mother liquor are obtained from the obtained 2nd crystallization product, and the 2nd crystal adduct circulates through this to said 1st crystallizing process. On the other hand, the 2nd mother liquor After making with the resultant which carries out reaction processing of this under existence of a basic catalyst, and contains an isopropenyl phenol and a phenol, the manufacture approach of bisphenol A which consists of a series of subprocesses which carry out the cyclic use of waste water as said isopropenyl phenol and a phenol is proposed. Since this approach does not circulate through the mother liquor obtained by carrying out crystallization of the resultant of a phenol and an acetone to the system of reaction of a phenol and an acetone using a subprocess, there is an advantage that are recording of a by-product or an impurity does not take place to the system of reaction, but in a subprocess, since are recording of by-products other than polyphenol or an impurity takes place, the purity of the 2nd crystal adduct obtained at a subprocess will become bad. Moreover, if it is going to raise the purity of the 2nd crystal adduct, it is necessary to make a part of 2nd mother liquor from a subprocess discharge out of a system but, and in this case, since bisphenol A, and a phenol and polyphenol are contained, there is a problem that loss of these useful components takes place in that mother liquor.

[0005]

[Problem(s) to be Solved by the Invention] This invention prevents effectively are recording of the by-product in the system of reaction, or an impurity, and it makes it the technical problem to offer the art of the mother liquor for removing efficiently the by-product and impurity which are contained in it from the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A while it offers the manufacture approach of bisphenol A which acquires bisphenol A of a high grade as crystal adduct with a phenol.

[0006]

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. According to this invention, the resultant acquired from the reaction process which makes an acetone and the phenol of an excessive amount react under existence of an acid catalyst, and makes bisphenol A generate, and this reaction process Namely, an acetone, The separation process divided into water, a phenol, and the phenol solution containing bisphenol A, The crystallizing process which deposits the crystal adduct of bisphenol A and a phenol from the phenol solution containing this bisphenol A, In the manufacture approach of bisphenol A which consists of a circulation process which circulates the mother liquor obtained at the crystallization product separation process and this crystallization product separation process of separating crystal adduct and a mother liquor from the crystallization product obtained with this crystallizing process to said reaction process (i) The distillation process which obtains the distillate which is made to distill 50 – 90% of the weight of the mother liquor which introduced these some circulation mother liquors [ at least ] into the distilling column, and was introduced into this distilling column, and contains a phenol, (ii) Reduced pressure evaporation of the product obtained at the heating process which heats the bottom of the distilling column obtained with this distillation process (i) at 200–350 degrees C under existence of a basic catalyst, and this (iii) heating process (ii) is carried out. The reduced pressure recovery process of obtaining the distillate steam containing a phenol and an isopropenyl phenol, (iv) The quenching process which the distillate steam obtained at this reduced pressure recovery process (iii) is contacted to the distillate obtained with the distillation process (i), and quenches it, (v) The manufacture approach of bisphenol A characterized by including the circulation process which circulates through the quenching object obtained at this quenching process (iv) at a reaction process is offered.

[0007] Moreover, it faces processing the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A according to this invention. (i) The distillation process which obtains the distillate which is made to distill 50 – 90% of the weight of the mother liquor which introduced these some mother liquors [ at least ] into the distilling column, and was introduced into this distilling column, and contains a phenol, (ii) Reduced pressure evaporation of the product obtained at the heating process which heats the bottom of

the distilling column obtained with this distillation process (i) at 200–300 degrees C under existence of a basic catalyst, and this (iii) heating process (ii) is carried out. The reduced pressure recovery process of obtaining the distillate steam containing a phenol and an isopropenyl phenol; (iv) The art of the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A characterized by including the quenching process which the distillate steam obtained at this reduced pressure recovery process (iii) is contacted to the distillate obtained with the distillation process (i), and quenches it is offered.

[0008] Next, this invention is explained, referring to a drawing. Drawing 1 is process drawing for manufacturing bisphenol A by this invention. drawing 1 -- setting -- 1 -- a reaction process and 2 -- a separation process and 3 -- a crystallizing process and 4 -- a crystallization product separation process and 5 -- a distillation process and 6 -- a heating process and 7 -- a reduced pressure recovery process and 8 -- strong acid mold ion-exchange-resin down stream processing -- each \*\*\*\*.

[0009] In the reaction process 1, the reaction of an acetone and the phenol of an excessive amount is performed under existence of an acid catalyst, and, thereby, bisphenol A is generated. Although mineral acids, such as a hydrochloric acid and a sulfuric acid, and the strong acid mold ion exchange resin which has a sulfonic group are used as an acid catalyst, use of strong acid mold ion exchange resin is desirable. The 8–20 mols of the amount of the phenol used are 10–18 mols in rate preferably to one mol of acetones. Reaction temperature is 50–90 degrees C. The resultant acquired at this reaction process 1 contains a coloring impurity and a coloring nature impurity further including by-products, such as bisphenol compounds, such as 2 which is the isomer of bisphenol A besides bisphenol A which is the specified substance, and 4'-bisphenol A, a tris phenolic compound, a polyphenol compound of the amount of macromolecules, a chroman compound, and water. if the typical presentation of this resultant is shown -- unreacted phenol:60–90wt% -- desirable -- 70 – 80wt% and unreacted acetone:0.1–2wt% -- desirable -- 0.5 – 1.5wt% and bisphenol A:15 – 30wt% -- desirable -- 18 – 25wt% and water:0.1 – 2wt% -- desirable -- 0.5 – 1.5wt% and byproduction polyphenol compound:2 – 15wt% -- it is 5 – 10wt% preferably. This resultant is introduced through Rhine 11 to the separation process 2.

[0010] The separation process 2 is a process which carries out separation processing of the resultant acquired at the reaction process 1, and is mainly divided into the phenol solution containing an acetone, water, a phenol, and bisphenol A, respectively. It circulates through the acetone separated at this separation process 2 at the reaction process 1 through Rhine 12, water is discharged through Rhine 13, a phenol is introduced into the crystallization product separation process 4 as a phenol for washing through Rhine 14, and the phenol solution containing bisphenol A is introduced into a crystallizing process 3 through Rhine 15. If the separation process 2 usually consists of distillation down stream processing including two or more distilling columns, and it is constituted so that it may separate into the specific component which described the resultant above, the separation process of arbitration can be used for it. The distillation processing schematic diagram of the resultant preferably adopted as drawing 2 as a separation process 2 of this invention is shown. drawing 2 -- setting -- 31 -- in the 1st distilling column and 32, the 4th distilling column and 35 show 36 and, as for the 2nd distilling column and 33, a strong acid mold ion-exchange-resin processor and 37 show a settler, as for the 3rd distilling column and 34.

[0011] The resultant acquired at the reaction process 1 which performs the reaction of a phenol and an acetone lets Rhine 38 pass, is introduced into the 1st distilling column 31 which constitutes the 1st distillation down stream processing, and is divided into the bottom material (I) containing an unreacted phenol, bisphenol A, and a by-product, and the overhead product (I) containing an unreacted phenol, an unreacted acetone, and water in this 1st distilling column 31.

[0012] if the component presentation of the overhead product (I) from the 1st distilling column is shown -- phenol:60 – 90wt% -- desirable -- 80 – 90wt% and acetone:2 – 20wt% -- desirable -- 5 – 10wt% and water:5 – 20wt% -- it is 5 – 10wt% preferably. if the component presentation of the bottom material (I) from the 1st distilling column is shown on the other hand -- phenol:50 – 80wt% -- desirable -- 65 – 75wt% and bisphenol A:18 – 30wt% -- desirable -- 20 – 25wt% and by-product:5 – 20wt% -- it is 5 – 10wt% preferably.

[0013] The overhead product (I) obtained in said 1st distilling column is introduced into the 2nd distilling column 32 which constitutes the 2nd distillation down stream processing through Rhine 40, and on the other hand, the bottom material (I) obtained in said 1st distilling column 31 and (the phenol solution containing bisphenol A) are extracted through Rhine 39, and are sent to a crystallizing process 3 through Rhine 15 of drawing 1 as a raw material for crystallization.

[0014] In the 2nd distilling column 32, distillation processing is performed under existence of an oily entrainer, and the overhead product (II) which consists of an acetone, water, and an entrainer is obtained. the component presentation of this overhead product (II) -- acetone:2 - 20wt% -- desirable -- 5 - 20wt% and water:10 - 30wt% -- desirable -- 15 - 25wt% -- it is -- entrainer:40 - 80wt% -- it is 50 - 70wt% preferably. A phenol is obtained from a bottom as a bottom material (II). the content of the acetone in the bottom material (II) of the 2nd distilling column 32 -- less than [ 5wt% ] -- it is zero % preferably. An entrainer adjusts the service condition of the 2nd distilling column, and it is desirable small quantity and to make 5 or less % of the weight exist at 1 or less % of the weight of a rate especially preferably in the bottom material of the 2nd distilling column. Thereby, the amount of phenol mixing to an overhead product can be reduced.

[0015] The overhead product (II) from the overhead of the 2nd distilling column 32 is introduced into the settler 36 which constitutes a standing process through Rhine 42, and is divided into the oily component which consists of an acetone and an entrainer here, and the aquosity component which consists of an acetone and water. An aquosity component is introduced into the 3rd distilling column 33 for the oily component separated by this settler 36 through Rhine 45 through Rhine 44, respectively. By dividing the overhead product (II) of the 2nd distilling column 32 into an oily component and an aquosity component by the settler 36, the overhead product (II) can be stably supplied to the 3rd distillation process. However, installation of this settler 36 is not necessarily needed, but an overhead product (II) can also supply the 3rd distilling column directly through Rhine 42. On the other hand, the bottom material (II) which consists of a phenol from the 2nd distilling column 32 passes along Rhine 41, and is introduced into the 4th distilling column 34 which constitutes the 4th distillation down stream processing through the strong acid mold ion-exchange-resin processor 35 if needed.

[0016] As an oily entrainer, 80-140 degrees C of 100-140-degree C hydrocarbon oils are preferably used for a boiling range. Toluene, ethylbenzene, a xylene, etc. are mentioned as an example of an entrainer. this entrainer -- the initial complement for [ said ] circulating through the 32nd distilling column 2 and the 3rd distilling column 33 from Rhine 43 on the occasion of the start up of the 2nd distilling column 32, as carried out -- the outside of a system -- a column -- after being supplied inside and dissociating by the settler 37 after a start up, it is returned to the 2nd distilling column 32 through Rhine 43.

[0017] In the 3rd distilling column 33 which constitutes the 3rd distillation down stream processing, an acetone is obtained as an overhead product (III), and this thing is extracted through Rhine 46 and it circulates through it at the reaction process 1 through Rhine 12 shown in drawing 1 . the water content in this circulation acetone -- less than [ 5wt% ] -- it is less than [ 3wt% ] preferably. On the other hand, although the bottom material (III) which consists of water and an entrainer is obtained from the bottom of the 3rd distilling column 33, this thing is introduced into the settler 37 which constitutes a standing process through Rhine 47, and is divided into an entrainer and water here. It circulates through an entrainer to the 2nd distilling column 32 through Rhine 43. On the other hand, water is discharged through Rhine 48. the acetone content contained during this wastewater -- less than [ 5wt% ] -- it is zero % preferably.

[0018] In the strong acid mold ion-exchange-resin processor 35, the strong acid mold ion exchange resin serves as a catalyst, and the coloring impurity contained in a bottom material (II) (phenol) and condensation nature impurities, such as a coloring impurity precursor, carry out a condensation reaction, and are changed into a tar-like high boiling point object. In this case, benzofuran etc. is mentioned as a condensation nature impurity. As strong acid mold ion exchange resin, the thing of a gel mold which has a sulfone radical is used, and such strong acid mold ion exchange resin is known well conventionally. For example, Amberlite and Amberlyst



which may come to hand from foam and HASU, the diamond ion which may come to hand from Mitsubishi Kasei Corp. can be used preferably. Processing of the bottom material (II) using this strong acid mold ion exchange resin can be carried out by the approach of circulating the packed column which contains strong acid mold ion exchange resin for a bottom material (II), the approach of putting in and agitating a bottom material (II) to the mixing vessel into which strong acid mold ion exchange resin was put, etc. processing temperature -- 45-150 -- it is 50-100 degrees C preferably. The contact time of strong acid mold ion exchange resin and a bottom material (II) is about 15 - 60 minutes preferably for 5 to 200 minutes. If moisture mixes into a bottom material (II) when processing a bottom material (II) using this strong acid mold ion exchange resin, the impurity removal effectiveness by strong acid mold ion exchange resin will fall. In this distillation approach, as mentioned above, in the 2nd distilling column 32, water is separated nearly completely as an overhead product component, and since water is not contained on parenchyma in the phenol obtained as a bottom material (II), strong acid mold ion-exchange-resin processing of that bottom material (II) is carried out smoothly.

[0019] If needed, it can mix with the bottom material (II) which lets Rhine 49 pass for a non-refined phenol, and passes along Rhine 41 in the strong acid mold ion-exchange-resin processor 35, and can introduce into it. An industrial use phenol, a mother liquor phenol, a washing waste fluid phenol which were obtained with the crystallizing process, etc. are mentioned to a non-refined phenol.

[0020] The processing product obtained with the strong acid mold ion-exchange-resin processor 35 is introduced into the 4th distilling column 34 through Rhine 50, and is divided into the overhead product (IV) which consists of a phenol here, and the bottom material (IV) which consists of tar-like high-boiling point matter. The service condition of this distilling column requires that a phenol and high-boiling point matter should be completely separable conditions, and it is necessary to perform it on the conditions which the high-boiling point matter does not mix into a phenol. The point with which it should mind in this case is making distillation processing temperature into 190 degrees C or less. Although an operating pressure will be set as arbitration if it is 190 degrees C or less in temperature, reduced pressure thru/or ordinary pressure of 50Torr(s) - 760Torr is usually adopted. Since disassembly of the high-boiling point matter etc. will become remarkable and the quality of a distillate phenol will be reduced if an operating temperature surpasses 190 degrees C, it is not desirable. the phenol introduced in this 4th distilling column 34 -- 99 % of the weight or more is distilled preferably 95% of the weight or more. The hue of the phenol obtained from the overhead of the 4th distilling column 34 is good, and the hue APHA is ten or less. This purification phenol is extracted through Rhine 52, and that part is introduced into the crystallization product separation process 4 through Rhine 14 shown in drawing 1 , and is used as a penetrant remover of the crystal adduct for obtaining high grade bisphenol A. [ at least ] Moreover, the cyclic use of waste water of this purification phenol can also be carried out to the reaction process 1 if needed. The bottom material (IV) extracted through Rhine 51 from the pars basilaris ossis occipitalis of the 4th distilling column 34 usually consists of mixture containing phenol:10-90 % of the weight and high-boiling point matter:10-60 % of the weight. Since the amount of this bottom material (IV) is little, it can be made to discharge out of a system as it is.

[0021] According to the separation process of the resultant shown in drawing 2 , since distillation in the 2nd distilling column 32 is performed under existence of an entrainer, the substantial whole quantity of water and an acetone is separable as an overhead product (II). And this overhead product (II) can be made to divide into water and an acetone nearly completely in the 3rd distilling column 33. That is, the substantial whole quantity of the acetone supplied to the 3rd distilling column 33 can be separated as an overhead product (III) of the 3rd distilling column, and there is no mixing of a parenchyma top acetone in the bottom material (III) of the 3rd distilling column 33. Consequently, there is no mixing of an acetone in wastewater extracted from a settler 37, and the problem of troublesome waste water treatment that an acetone is removed from that wastewater is solved. Moreover, also in the acetone separated from the 3rd distilling column 33 as an overhead product (III), since it is not mixed, reuse of an acetone is also easy for most water.

[0022] Other distillation processing schematic diagrams employable as drawing 3 as a separation process 2 of this invention are shown. In drawing 3, in 31, the 3rd distilling column and 34 show the 4th distilling column, and, as for the 1st distilling column and 32, 35 shows a strong acid mold ion-exchange-resin processor, as for the 2nd distilling column and 33.

[0023] The product obtained at the reaction process 1 which performs the reaction of a phenol and an acetone lets Rhine 38 pass, is introduced into the 1st distilling column 31 which constitutes the 1st distillation down stream processing, and is divided into the bottom material (I) which contains an unreacted phenol, bisphenol A, and a by-product here, and the overhead product (I) containing an unreacted phenol, an unreacted acetone, and water. the 1st distilling column 31 -- the phenol content in the overhead product (I) -- less than [ 40wt% ] -- it is operated so that it may become the range not more than 30wt% preferably. Thereby, the water content in \*\*\*\*\* (II) obtained from the 2nd distilling column 32 can be controlled a 5wt% less or equal, especially less than [ 2wt% ]. if the component presentation of the overhead product (I) of the 1st distilling column 31 is shown -- less than [ phenol:40wt% ] -- desirable -- less than [ 30wt% ] and acetone:20 - 45wt% -- desirable -- 30 - 40wt% and water:20 - 45wt% -- it is 30 - 40wt% preferably. if the component presentation of the bottom material (I) of the 1st distilling column 31 is shown on the other hand -- phenol:55 - 80wt% -- desirable -- 65 - 75wt% and bisphenol A:18 - 30wt% -- desirable -- 20 - 25wt% and by-product:5 - 15wt% -- it is 6 - 10wt% preferably. The overhead product (I) obtained in said 1st distilling column 31 is introduced into the 2nd distilling column 32 which constitutes the 2nd distillation down stream processing through Rhine 40, and, on the other hand, the bottom material (I) obtained in said 1st distilling column 31 is introduced into the 4th distilling column 34 through Rhine 39.

[0024] In the 2nd distilling column 32, an acetone is obtained as an overhead product (II), and this thing is extracted through Rhine 46 and it circulates through it at the reaction process 1 through Rhine 12 shown in drawing 1. the water content in this circulation acetone -- less than [ 10wt% ] -- it is less than [ 5wt% ] preferably. On the other hand, the bottom material (II) which consists of mixture of a phenol and water is obtained from the bottom of the 2nd distilling column 32, and this thing is introduced into the 3rd distilling column 33 through Rhine 47. the component presentation of the bottom material (II) of the 2nd distilling column 32 -- phenol:40 - 60wt% -- desirable -- 40 - 50wt% and water:40 - 60wt% -- it is 50 - 60wt% preferably, and the content of an acetone is less than [ 1wt% ].

[0025] In the 3rd distilling column 33 which constitutes the 3rd distillation down stream processing, water is obtained as an overhead product (III) and this thing is discharged through Rhine 48. On the other hand, although the bottom material (III) which consists of a phenol is obtained from the bottom of the 3rd distilling column 33, after this thing is processed with the strong acid mold ion-exchange-resin processor 35 through Rhine 41, it is introduced into the 4th distilling column 34 which constitutes the 4th distillation down stream processing. Moreover, if needed, to the bottom material (III) of this 3rd distilling column 33, it can add through Rhine 49, and a non-refined phenol can be introduced into the strong acid mold ion-exchange-resin processor 35 at it. In this case, as a non-refined phenol, an industrial use phenol, a mother liquor phenol, a washing waste fluid phenol which are obtained with a crystallizing process, etc. are mentioned.

[0026] In the strong acid mold ion-exchange-resin processor 35, the strong acid mold ion exchange resin serves as a catalyst, and condensation nature impurities contained in a phenol, such as a coloring impurity and a coloring impurity precursor, carry out a condensation reaction, and are changed into a tar-like high boiling point object. The processing product obtained with the strong acid mold ion-exchange-resin processor 35 is introduced into the 4th distilling column 34 which constitutes the 4th distillation down stream processing through Rhine 50, and a phenol is acquired as an overhead product (IV) here. Moreover, the bottom material (I) and (the phenol solution containing a bisphenol) of the 1st distilling column 31 are introduced into this 4th distilling column 34 through Rhine 39. In this 4th distilling column 34, although a phenol is distilled from that overhead, the hue of this phenol is good and that hue APHA is ten or less. As this purification phenol is shown in drawing 1, it circulates at least through that part at the crystallization product separation process 4 through Rhine 14, and it is used as a penetrant

remover of the crystal adduct for obtaining high grade bisphenol A. Moreover, the cyclic use of waste water of this purification phenol can be carried out to the reaction process 1 if needed. The bottom material (IV) extracted through Rhine 51 from the pars basilaris ossis occipitalis of the 4th distilling column 34 usually, a bisphenol -- 15 - 30wt% -- preferably including 20 - 25wt%, preferably, including a phenol 50 to 80% of the weight, 65 to 75% of the weight, a by-product is further included at 6 - 10% of the weight of a rate preferably five to 15% of the weight, and as shown in drawing 1, it is introduced as a raw material for crystallization through Rhine 15 to a crystallizing process 3. In addition, the bottom material (I) of the 1st distilling column 31 can also be introduced to a crystallizing process 3 as it is, without introducing into the 4th distilling column 34.

[0027] According to the separation process of the resultant shown in drawing 3, by holding the phenol content in the overhead product (I) obtained from the 1st distilling column 31 to 40 or less % of the weight, the substantial whole quantity of the acetone supplied to the 2nd distilling column 32 can be separated as an overhead product (II) of the 2nd distilling column, and there is no mixing of a parenchyma top acetone in the bottom material (II) of the 2nd distilling column 2. Consequently, in the 3rd distilling column 33, there is no mixing of an acetone in the water separated as that overhead product (III), and the problem of troublesome waste water treatment that an acetone is removed from that sejunction water is solved. Moreover, according to this separation process, in the 3rd distilling column, since an acetone does not exist, that distillation actuation can be performed efficiently.

[0028] A crystallizing process 3 is a process which the solution containing bisphenol A obtained at the separation process 2 as was the above is cooled [ process ], and deposits the crystal adduct of bisphenol A and a phenol. In this case, 35-80 degrees C of crystallization temperature are 45-70 degrees C preferably. The crystallization product (crystal adduct slurry) obtained with this crystallizing process is introduced into the crystallization product separation process 4 through Rhine 16 in drawing 1. Although a crystallizing process 3 can consist of one or more crystallization phases, it shows the crystallization schematic diagram about one example of the crystallizing process to drawing 4. drawing 4 -- setting -- 55 -- an outer case and 56 -- a container liner and 57 -- a microcrystal adduct solution tank and 58 -- a condensator and 59 -- a heater, and 60 and 61 -- a pump and A -- crystallization -- a column is shown. crystallization -- a column -- A has the double cylinder structure which inserted the container liner 56 which has opening in the upper part into the outer case 55 of sealing structure. the sealing structure as used in this specification -- crystallization -- a column is not in an atmospheric-air disconnection condition, but the condition that the seal is carried out in inert gas is said. crystallization -- a column -- A is atmospheric-air disconnection -- crystallization -- a column -- while a part of oxygen in atmospheric air is absorbed by the inner slurry and worsening the hue of adduct, in latter processing, it has a bad influence, and it becomes impossible for adduct \*\*\*\*\* of high quality to obtain bisphenol A of high quality further therefore, crystallization -- a column -- in A, in order to prevent mixing of oxygen, it will be necessary to carry out a seal in inert gas In this case, if mixing of oxygen can be prevented, it is not necessary to be necessarily the sealing proof-pressure container which can bear high pressure. moreover, crystallization -- a column -- in A, after preparing a container liner on the medial axis of the revolution style of an internal slurry rather than preparing a direct extraction hole in the outer case section, raising the revolution style of a slurry to the upper part, carrying out overflow of the slurry from opening of the container liner upper part and dropping the interior of a container liner, it is good to take the approach of extracting from a container liner pars basilaris ossis occipitalis. Thereby, sufficient residence time is securable to an adduct particle with uniform mixing to the introduced circulation slurry.

[0029] In order to carry out a crystallizing process according to the crystallization schematic diagram shown in drawing 4 first, some phenol solutions containing bisphenol A which is the processed raw material extracted through Rhine 15 of drawing 1 from the separation process 2 -- Rhine 62 and Rhine 63 -- passing -- crystallization -- a column, while being filled up in A the pars basilaris ossis occipitalis of a container liner 56 to Rhine 64 -- passing -- a phenol solution -- an extract and this -- Rhine 65, a pump 60, Rhine 66, a condensator 58, Rhine 67, and Rhine

63 -- letting it pass -- crystallization -- a column -- it is made to circulate continuously in the outer case of A lower part this actuation -- crystallization -- a column -- it is cooled, crystal adduct carries out crystallization of the phenol solution in A, and the slurry containing crystal adduct is generated. the crystallization as it was the above, after this slurry was extracted from the pars basilaris ossis occipitalis of a container liner 56, and being cooled with the condenser 58 -- a column -- it comes to circulate in the outer case 55 of A lower part. moreover, the pars basilaris ossis occipitalis of a container liner 56 to a part of slurry -- Rhine 64, Rhine 68, a pump 61, Rhine 69, a heater 59, a tank 57, and Rhine 70 and 71 -- passing -- crystallization -- a column -- it is made to circulate continuously in the outer case 55 of A lower part by this actuation, the microcrystal adduct particle in the slurry extracted from the pars basilaris ossis occipitalis of a container liner 56 dissolves by the tank 57 -- having -- a slurry with low microcrystal adduct particle content -- crystallization -- a column -- it circulates in A. consequently, crystallization -- a column -- the content of the microcrystal adduct particle in A comes to decrease.

[0030] next, the phenol solution which contains bisphenol A extracted through Rhine 15 from the separation process 2 in such a condition -- Rhine 62 and Rhine 63 -- letting it pass -- crystallization -- a column -- while introducing in the outer case 55 of A lower part, a product slurry is extracted through Rhine 73 from the pars basilaris ossis occipitalis of a container liner 56. In this case, when this slurry can be passed by the gravity flow to the following crystallization product separation process, it extracts using Rhine 73 in this way, but when that is not right, that part can also be extracted from regurgitation Rhine 74 of a pump 61. Moreover, a part of slurries with little microcrystal content can be collected from Rhine 72, and this can also be made into a product crystal adduct slurry. These crystal adduct slurries can perform the still more nearly same crystallization processing as the above if needed.

[0031] The slurry passing through the slurry passing through Rhine 63 which carried out the temperature reduction, and Rhine 70 and 71 which carried out the temperature rise is faced making it introduce in an outer case 55, and is better than the outer case lower part in an outer case to introduce so that the revolution style of the same sense may be produced. In this case, preferably, it introduces so that it may become a tangential direction to outer case inner skin, and it carries out so that those introductory locations may differ. if an introductory location is too near -- the turbulence of local flow -- being generated -- a smooth revolution style -- it cannot obtain -- becoming -- moreover, crystallization -- it is not desirable from the structure of a column, and a strong field. Therefore, the introductory location of these two slurries is good to carry out in the location which expressed with the include angle and was preferably separated from the central point of an outer case 90 to 180 degrees. Furthermore, if it is for the revolution style of the same sense to arise, the introductory location of two slurries does not necessarily need to be on the same horizontal plane, and even if there is a difference of some height, it will not interfere in the outer case lower part at least. As it is the above, if each slurry passing through Rhine 63 and Rhine 70 and 71 is introduced so that the revolution style of the same sense may be produced in an outer case, this revolution style will go up the inside of an outer case 55 to the upper limit section of a container liner 56, and will descend the inside of a container liner 56 from up opening of a container liner 56, and will be extracted through Rhine 64 from the pars basilaris ossis occipitalis of that container liner. The following effectiveness can be acquired by producing such a revolution style in an outer case 55.

- (1) Two liquid flows of different temperature are effectively mixable to homogeneity.
- (2) Since channeling of a slurry is prevented and the slurry concentration in an outer case becomes homogeneity, the nonuniformity of the residence time within the outer case of a crystal adduct particle can be lost.
- (3) Sufficient linear velocity which is sufficient for preventing sedimentation deposition within the outer case of a crystal adduct particle can be obtained.

[0032] Moreover, a part of slurry extracted from container liner 56 pars basilaris ossis occipitalis as mentioned above Rhine 64, Rhine 68, a pump 61, a heater 59, a tank 57, and Rhine 70 and 71 -- letting it pass -- crystallization -- a column, when circulating A From dissolution disappearance of the microcrystal adduct in a slurry being carried out within a tank 57 It

circulates to A. the slurry containing the big and rough crystal adduct of fixed magnitude -- Rhine 70 and 71 -- passing -- crystallization -- a column -- this -- crystallization -- a column -- the particle size of the crystal adduct contained in A arranges -- having -- crystallization -- a column -- in A, microcrystal adduct particle content is low and the high crystal adduct of big and rough crystal adduct particle content is generated. crystallization -- a column -- since the specific surface area is large, the microcrystal adduct in A shows adsorbent [ high ] to a coloring causative agent. therefore, crystallization -- a column -- the good crystal adduct of a hue can be obtained by decreasing the microcrystal adduct particle content in the crystal adduct obtained by A as much as possible. The good high grade crystal adduct of a hue can be manufactured by holding preferably microcrystal adduct particle content with a particle size [ in crystal adduct ] of 100 micrometers or less to 20 or less % of the weight 30 or less % of the weight.

[0033] temperature with the temperature of the phenol solution containing bisphenol A supplied from Rhine 62 higher about 1-20 degrees C than the saturation temperature of crystal adduct -- it is -- crystallization -- a column -- the temperature of A is 45-70 degrees C. In a condensator 58, 5-degree-C or less extent descent of about 10 degrees C or less of the slurries which circulate through Rhine 65, a pump 60, a condensator 58, and Rhine 63 is preferably carried out in the temperature. crystallization -- a column -- the residence time of the phenol solution in A is 0.5 - 5 hours preferably for 0.5 to 10 hours. On the other hand, in the heater 59, the slurry introduced into the microcrystal adduct solution tank 57 through Rhine 68, a pump 61, Rhine 69, and a heater 59 goes up the temperature by about 0.5-5 degrees C, and is held at the microcrystal solution tank 57. The residence time of the phenol solution in this tank 57 is about 3 - 15 minutes.

[0034] Crystal adduct with a particle size of 100 micrometers or less is dissolved into the microcrystal solution tank 57. Crystal adduct particle content with a particle size [ in the crystal adduct in the slurry passing through Rhine 70 ] of 100 micrometers or less is 20 or less % of the weight preferably 30 or less % of the weight.

[0035] According to said crystallization method, the good crystal adduct of a hue with low microcrystal adduct particle content can be made to generate efficiently. This crystal adduct gives good bisphenol A of a hue by from now on carrying out separation removal of the phenol.

[0036] The crystal adduct slurry (crystallization product) obtained with said crystallizing process 3 is sent to the crystallization product separation process 4. In this crystallization product separation process 4, a crystal adduct slurry is divided into crystal adduct and a mother liquor, and washing processing of the crystal adduct is carried out, using the purification phenol extracted through Rhine 14 from the separation process 2 as a penetrant remover. And if needed, with a phenol [ finishing / washing ], the separated mother liquor is extracted from the crystallization product separation process 4 through Rhine 17, and it circulates through it at the reaction process 1. In this case, at least, it introduces into the mother liquor purification process of a circulation mother liquor which usually carries out the postscript of this one to 20% of the weight in part, and processes. And the mother liquor by which purification processing was carried out makes the reaction process 1 circulate through this again.

[0037] In the crystallization product separation process 4, when carrying out filtration processing of the crystal adduct slurry and separating crystal adduct from a mother liquor, it is desirable that make a part of microcrystal adduct component [ at least ] with a particle size of 100 micrometers or less shift to a filtrate (mother liquor) side among the crystal adducts contained in the slurry, and the rate of a microcrystal adduct component with a particle size of 100 micrometers or less obtains 15 or less % of the weight of big and rough crystal adduct preferably 20 or less % of the weight. In this case, in order to make a microcrystal adduct component shift to a filtrate side, selection of a filter (filtering medium) and selection of a filtration operating condition can perform. Generally as a filter, 100-300 micrometers of 150-250-micrometer things are preferably used for the \*\*\*\*. moreover, the crystal adduct from which the amount of shift of the microcrystal adduct component is obtained by the filtration processing when making a microcrystal adduct component shift to a filtrate side according to a filtration operating condition -- the frequency which carries out a back wash can adjust the thickness of a cake, and its cake.

[0038] Although the crystal adduct which is the above, and was made and obtained is a high-definition thing which has a low impurity content in itself, it can raise that grade further by washing this crystal adduct further with the purification phenol extracted through Rhine 14 from the separation process 2. Washing of the crystal adduct by the purification phenol should just be the approach that contact to crystal adduct and a purification phenol may fully be attained. In solid-liquid separators, such as a filter for separating for example, crystal adduct, and a centrifugal separator, this washing processing can also wash the crystal adduct to which the approach of introducing a purification phenol in that solid-liquid separator, and washing it and the little mother liquor discharged from a solid-liquid separator adhere with a purification phenol in another mixing vessel, after removing a mother liquor from crystal adduct. The operating rates of a purification phenol to crystal adduct are more than the 100 weight sections preferably more than 50 weight sections to the crystal adduct 100 weight section.

[0039] Although the crystal adduct by which washing processing was carried out with the purification phenol is a crystal which consists of an equimolar presentation of bisphenol A and a phenol, this thing can remove a phenol at a direct dephenolation process delivery and here, can collect product bisphenol A of a high grade, and after processing at a crystallizing process and a crystallization product separation process again, it can collect delivery and product bisphenol A of a super-high grade at a dephenolation process. Removal of a phenol can be conventionally performed from crystal adduct by approaches, such as a well-known approach, for example, distillation, an extract, and steam stripping.

[0040] According to the above mentioned filtration of a crystal adduct slurry and washing processing of crystal adduct, the good crystal adduct of the thermal stability which can remove efficiently the adsorbent high impurity of the coloring matter adhering to a crystal adduct front face, the coloring nature matter, etc., and is excellent in a hue by this, and cannot produce coloring easily can be obtained easily. Moreover, it is the high-definition thing which bisphenol A which removes a phenol and is obtained from this crystal adduct is also excellent in a hue, and cannot produce coloring easily.

[0041] Although the cyclic use of waste water of the mother liquor obtained from the crystallization product separation process 4 as was the above is carried out to the reaction process 1 through Rhine 17 and Rhine 19 which were shown in drawing 1, a part of the circulation mother liquor [ at least ] is extracted from Rhine 17, and purification processing is carried out by the (i) distillation process 5, (ii) heating process 6, the reduced pressure recovery process 7, and the strong acid mold ion-exchange-resin down stream processing 8 through Rhine 18. Although the heating process 6 and the reduced pressure recovery process 7 can be carried out independently, respectively, it is desirable to carry out to coincidence using a reactor.

[0042] The processing schematic diagram about one example of the purification art of the mother liquor extracted through drawing 1 Rhine 17 and 18 by drawing 5 is shown. drawing 5 -- setting -- 5 -- a phenol distilling column and D -- a reaction vessel 6 and reduced pressure evaporation -- the reactor and R which have a column 7 -- strong acid mold ion exchange resin -- a column is shown. A raw material mother liquor is introduced into the phenol distilling column 5 through Rhine 18. In this case, as a raw material mother liquor, some mother liquors [ at least ] obtained at the crystallization product separation process 4 can be used. In crystallization processing of the phenol solution containing bisphenol A, although two or more steps of crystallizing processes and the solid-liquid-separation process of a crystallization product are adopted and two or more sorts of mother liquors (phenol solution) are usually obtained according to it, by this invention, the thing of the arbitration of these mother liquors can be used as a raw material mother liquor. The desirable raw material mother liquor used by this invention is a mother liquor separated from the 1st crystallization product obtained with the crystallizing process of the 1st step. The coloring nature impurity which usually changes into the coloring matter the mother liquor separated from this crystallization [ 1st ] product with heating of coloring nature impurity:2 or less % of the weight aldehydes, such as a chroman compound, a quinone, etc. polyphenol:1-5% of the weight of others which contain 4[ 2 and ]-bisphenol A fail:85

% of the weight and bisphenol A: 5-10% of the weight: Contain a minute amount.

[0043] the phenol distilling column 5 -- temperature: -- it is preferably operated by 100-200 degrees C on 120-185-degree-C, pressure: 50 torr - ordinary pressure conditions. In this phenol distilling column 5, the raw material mother liquor introduced from Rhine 18 is desirable 50 to 90% of the weight, and 65 - 85 % of the weight is distilled. If the amount of distillates increases more than this range, it will become hyperviscosity and problems, such as bottom material solidification and the Rhine lock out, will arise, on the other hand, if fewer than this range, the concentration of a phenol will become high and the problem of the processing effectiveness and thermal efficiency in a heating process or a reduced pressure recovery process falling will arise. After the distillate steam from the phenol distilling column 5 is condensed with the condenser 85 attached to this distilling column, that part is returned to a distilling column 5 through Rhine 86 as reflux, and the condensate (distillate) of the remainder is introduced into the reduced pressure condenser 90 attached to Reactor D through Rhine 87. The distillate passing through this Rhine 87 consists of phenol 100% mostly. On the other hand, that bottom is extracted through Rhine 81 from the pars basilaris ossis occipitalis of the phenol distilling column 5, this bottom is introduced into the reaction vessel 6 of the pars basilaris ossis occipitalis of Reactor D through Rhine 84 with the basic catalyst supplied through Rhine 83, and evaporation recovery processing of the concentration mother liquor containing the product generated by this reaction is performed to the reaction and coincidence of the reactant component contained in it here. In addition, supply of a basic catalyst can also be directly performed to the reaction vessel 6 of Reactor D. the bottom extracted through Rhine 81 from the pars basilaris ossis occipitalis of the phenol distilling column 5 -- usually -- phenol: -- ten to 50% of the weight, it is 15 - 30 % of the weight preferably, and the remainder consists of bisphenol A, 2, 4'-bisphenol A, other polyphenol, and other impurities.

[0044] In Reactor D, while the pyrolysis of the polyphenol contained in a concentration mother liquor in the reaction vessel 6, such as a bisphenol and a tris phenol, is carried out by operation of a basic catalyst and it is converted into an isopropenyl phenol and a phenol, the polycondensation reaction of impurities, such as a chroman compound, occurs and an impurity is changed into a high boiling point object. As a basic catalyst, the hydroxide of alkaline earth metal, such as the hydroxide of alkali metal, such as sodium and a potassium, an oxide, a carbonate, various phenol salts, calcium, and magnesium, an oxide, a carbonate, various phenol salts, etc. are mentioned. The operating rate of this basic catalyst is 0.01 - 0.5 % of the weight preferably 0.005 to 0.8% of the weight to all the polyphenol containing bisphenol A in the concentration mother liquor extracted through Rhine 81.

[0045] Reactor D -- a pars basilaris ossis occipitalis -- a reaction vessel 6 -- having -- the reaction-vessel top -- reduced pressure evaporation -- it has the structure which set up the column 7. this reactor D -- bottom (reaction vessel) temperature: 200-350 degree C -- desirable -- 220-300 degrees C and a column -- internal pressure: 5 torr - ordinary pressure -- it is preferably operated on 10-150-torr conditions. Rhine 91 after carrying out mixed contact with the distillate which the distillate steam containing the phenol and isopropenyl phenol which were extracted through Rhine 89 from the crowning of Reactor D was introduced into the reduced pressure condenser 90 attached to Reactor D, and took Rhine 87 from the phenol distilling column 5, and was introduced here and quenching -- passing -- strong acid mold ion exchange resin -- a column -- it is introduced into R. 45-150 degrees C of temperature of the distillate sent to the reduced pressure condenser 90 through Rhine 87 from the phenol distilling column 5 are 50-110 degrees C preferably. moreover, the weight ratio to the distillate steam with which the amount of the distillate passing through Rhine 87 passes along Rhine 89 -- 1-20 -- it is 2-15 preferably. The component of the distillate steam extracted from Reactor D through Rhine 89 is the impurity of a phenol, an isopropenyl phenol, bisphenol A, and others. the liquid with which the bottom (reaction mixture) extracted from Reactor D through Rhine 88 is supplied to Reactor D through Rhine 84 -- receiving -- a weight ratio -- 0.05-0.5 -- it is 0.05-0.4 preferably, and while a high boiling point object (it has the boiling point higher than bisphenol A) is condensed by this bottom, the matter of coloring nature is condensed. the mixed liquor in the reduced pressure condenser 90 -- Rhine 91 -- passing -- strong acid mold ion exchange resin -- a column -- it



is introduced into R. this strong acid mold ion exchange resin -- a column -- bisphenol A is generated by the reaction of the isopropenyl phenol and phenol which are contained in mixed liquor in R. The product containing this bisphenol A is discharged through Rhine 92, and is introduced into circulation mother liquor Rhine 19 or the reaction process 1 shown in drawing 1 through Rhine 25.

[0046] As strong acid mold ion exchange resin, the thing of a gel mold which has a sulfone radical is used, and such strong acid mold ion exchange resin is known well conventionally. For example, Amberlite and Amberlyst which may come to hand from Ioam and HASU, the diamond ion which may come to hand from Mitsubishi Kasei Corp. can be used preferably. In the reaction of the mixed liquor using this strong acid mold ion exchange resin, 45-130 degrees C of that reaction temperature are 50-100 degrees C preferably, and contact time is 15 - 120 minutes preferably for 5 to 200 minutes. When reacting the mixed liquor using this strong acid mold ion exchange resin, the moisture in mixed liquor is preferably carried out to 0.1 or less % of the weight 0.5 or less % of the weight. strong acid mold ion exchange resin -- the component of the resultant extracted through Rhine 92 from Column R -- phenol:85-95 % of the weight and bisphenol A: -- five to 15% of the weight, it is other impurity:minute amounts and coloring nature is preferably low five to 10% of the weight. As shown in drawing 1 , the cyclic use of waste water of this thing is carried out to the reaction process 1 through Rhine 25. Moreover, if needed, concentration crystallization of the part can be carried out, and it can consider as bisphenol A and phenol crystal adduct. in addition, strong acid mold ion exchange resin -- a column -- R is not necessarily needed but the direct reaction process 1 can be made to circulate through the overhead product of the reaction distillation D

[0047] As shown in drawing 6 , as for Reactor D, it is desirable to attach and use a heat treatment equipment A and the stagnation tub B. In operation of such a reactor D, it passes along Rhine 96 from the reaction vessel 6 of the pars basilaris ossis occipitalis of Reactor D, and a part of the bottom material is extracted, and after a part of the extracted bottom material is introduced into a heat treatment equipment A through Rhine 97 as the 1st circulation liquid and it receives heat-treatment here, it circulates to the reaction vessel 6 of Reactor D through Rhine 94 and Rhine 95. In a heat treatment equipment A, the 200-350 degrees C of the 1st circulation liquid are preferably heated by the temperature of 230-300 degrees C under existence of a basic catalyst. With this heating, the polyphenol contained in the 1st circulation liquid undergoes the above mentioned pyrolysis reaction. The residence time of the 1st circulation liquid in a heat treatment equipment A is 1 - 20 minutes preferably for 1 to 30 minutes. On the other hand, a part of bottom material extracted from the pars basilaris ossis occipitalis of the reaction distilling column D circulates to the reaction vessel 6 of Reactor D as the 2nd circulation liquid through Rhine 98, Rhine 99, the stagnation tub B, and Rhine 100. In the stagnation tub B, the 200-300 degrees C of the 2nd circulation liquid are preferably held for 10 - 100 minutes in the temperature of 220-280 degrees C for 5 to 120 minutes. When the depolymerization of the polyphenol contained in a mother liquor is inadequate, while that depolymerization advances further by this stagnation processing, when heavy-izing of a coloring causative agent, for example, a chroman compound, is inadequate, that heavy-ization advances further and the effectiveness of being changed into the easy high-boiling point tarry material of separation is acquired. the concentration mother liquor 100 weight section by which the circulating load of the 1st circulation liquid is supplied to Reactor D through Rhine 100 -- receiving -- the 50 - 5000 weight section -- it is -- on the other hand -- the circulating load of the 2nd circulation liquid -- the same -- the 10 - 10000 weight section -- it is the 50 - 5000 weight section preferably.

[0048] In the art of the above mentioned mother liquor, the impurity contained in a mother liquor lets Rhine 23 ( drawing 1 ) or Rhine 88 ( drawing 5 , drawing 6 ) connected with the bottom or reaction vessel 6 of Reactor D pass, and is discharged as a concentration impurity. The by-product of a high-boiling point and the condensate of a condensation nature impurity are contained rather than bisphenol A, and further, when the ion exchange resin which has the strong acid nature matter of a high-boiling point, for example, a sulfonic group, as a catalyst in the reaction process 1 is used, the sulfonation object isolated from that catalyst is contained in



this concentration impurity. Therefore, according to the art of the above mentioned mother liquor, separation removal of each high boiling point object (sulfonation object etc.) of the catalyst origin further used at the reaction process 1 is carried out from a mother liquor in the polyphenol compound contained in the mother liquor, a coloring impurity, a coloring nature impurity, and the condition of having been condensed. And by circulating through the mother liquor from which it did in this way and the by-product and the impurity were removed at the reaction process 1 again, loss of the useful component contained in a mother liquor can be suppressed, and are recording of the by-product in the system of reaction and an impurity can be prevented, consequently bisphenol A which is a high grade and by which coloring was prevented can be obtained.

[0049]

[Example] Next, an example explains this invention to a detail further.

[0050] (I) -- the reaction process 1 -- according to the well-known approach, the reaction of an acetone and a phenol was conventionally performed under existence of the ion exchange resin which has a sulfonic group. In this case, 14 mols of phenols per one mol of acetones were used. The reaction was performed at 60 degrees C. Thus, the presentation of the acquired resultant was as follows.

Bisphenol A: 0.8wt% water : 1.0wt% phenol : 73.6wt% bisphenol A: 18.8wt% others : 5.8wt% [0050]

(II-1) Separation process ( drawing 2 )

According to the schematic diagram shown in drawing 2 , distillation processing of the phenol and acetone resultant which were acquired at said reaction process 1 was carried out. In this case, relation with Rhine or equipment shown in drawing 2 shows the used main operating conditions below.

(1) The overhead product passing through Rhine 40 (I)

(i) Component presentation acetone : 5.8wt% phenol : 7.2wt% water : 86.1wt% others : Overhead product passing through 0.9wt% (2) Rhine 42 (II)

(i) Component presentation acetone : 18.5wt% water : 22.5wt% entrainer : 55.6wt% others : Bottom material passing through 3.4wt% (3) Rhine 41 (II)

(i) Component presentation phenol : 99.0wt% entrainer : 0.5wt% others : Overhead product passing through 0.5wt% (4) Rhine 46 (III)

(i) Component presentation acetone : 85.1wt% water : 1.0wt% others : (Wastewater i) component water of constitution passing through 13.9wt% (5) Rhine 48 : 99.95wt% phenol : 0.05wt% [0051] (II-2)

2) Separation process 2 ( drawing 3 )

According to the equipment schematic diagram shown in drawing 3 , the resultant of the phenol and acetone which were obtained at said reaction process 1 was processed. In this case, relation with Rhine or equipment shown in drawing 3 shows the used main operating conditions below.

(1) The overhead product passing through Rhine 40 (I)

(i) Component presentation acetone : 29.0 wt% water : 38.8 wt% phenol : 29.9 wt% others : 2.3 Overhead product passing through wt% (2) Rhine 46 (II)

(i) Component presentation acetone : 89.7 wt% water : 2.1 wt% others : 8.2 Bottom material passing through wt% (3) Rhine 47 (II)

(i) Component water of constitution : 55.5 wt% phenol : 44.2 wt% others : 0.3 Overhead product passing through wt% (4) Rhine 48 (III)

(i) Component water of constitution : 99.7 wt% phenol : 0.2 wt% others : 0.1 Bottom material passing through wt% (5) Rhine 41 (III)

(i) Component presentation phenol : 99.0 wt% others : 1.0 wt% [0053] (III) Crystallizing process 3 ( drawing 4 )

According to the equipment schematic diagram shown in drawing 4 , crystallization processing of the phenol solution containing bisphenol A was carried out, and the slurry (crystallization product) containing crystal adduct was obtained. Relation with Rhine or equipment shown with the sign in drawing 4 shows the main operating conditions in this case below.

(1) component presentation bisphenol A [ of the feed in Rhine 62 ]: -- 22-% of the weight phenol: -- 74 % of the weight -- in addition to this -- : -- 4-% of the weight (2) crystallization -- column A (i) temperature: -- 50-degree-C (ii) residence-time: -- 120-minute (3) crystallization -- a

column -- it attached to A -- microcrystal adduct solution tank 57 (i) -- temperature: -- 51-degree-C (ii) residence-time: -- the rate of a particle with a particle size [ in the crystal adduct separated from the slurry obtained through Rhine 73 in said experiment for 6 minutes ] of 100 micrometers or less was 20 % of the weight.

[0054] (IV) -- the crystal adduct obtained after carrying out filtration under reduced pressure with the filter which set the filter cloth which has a 106-micrometer opening for the crystal adduct slurry obtained by carrying out crystallization processing of the phenol solution containing crystallization product separation process 4 bisphenol A, holding slurry temperature at 50 degrees C -- the purification phenol which was able to be obtained from the separation process 2 of the above (II-1) washed the cake. The rate of the microcrystal adduct component 100 micrometers or less in this washing crystal adduct was 5 % of the weight. It was 10APHA(s), and the concentration of a coloring impurity was remarkable and that of the melting color of this crystal adduct was low. Moreover, the concentration of the chroman compound (coloring nature impurity) contained in this crystal adduct was 100wtppm(s).

[0055] (V) Purification processing of the mother liquor separated from the crystallization product ( drawing 5 )

According to the equipment schematic diagram shown in drawing 5 , the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A was processed. In this case, the used main operating conditions are shown below in connection with Rhine or equipment shown in drawing 5 .

(1) (mother liquor i) component presentation phenol: passing through Rhine 18 -- 86.3-% of the weight bisphenol A: -- 7.7 % of the weight 2 and 4'-bisphenol A: 2.4 % of the weight -- in addition to this -- an or more [ : 3.6 % of the weight (ii) hue APHA: ] 500(2) phenol distilling column (5) [ , such as a tris phenol, polyphenol, a coloring impurity, and a coloring nature impurity, ]

(i) -- bottom temperature: -- 170-degree-C (ii) pressure : (Distillate i) component presentation phenol: passing through 170-torr (3) Rhine 11 -- bottom material (concentration mother liquor) passing through 99.8-% of the weight or more (ii) hue APHA: 10 (4) Rhine 81

(i) -- component presentation phenol: -- 14.8-% of the weight bisphenol A: -- 48.5 % of the weight 2 and 4'-bisphenol A: -- the concentration mother liquor which passes along addition: Rhine 81 of the basic catalyst (NaOH) in or more [ : 21.9 % of the weight (ii) hue APHA: ] 500 (5) Rhine 83, such as a tris phenol, polyphenol, a coloring impurity, and a coloring nature impurity, in addition to this 14.8% of the weight -- receiving -- 0.05-% of the weight reaction [ (6) ] \*\*\*\*\* (D)

(i) -- bottom temperature: -- 250-degree-C (ii) pressure : distillate (steamy i) component presentation phenol: passing through 40-torr (7) Rhine 89 -- a 92.6-% of the weight isopropenyl phenol -- and -- in addition to this -- : -- 7.4-% of the weight (ii) hue APHA: 200 (8) Rhine 88 (Bottom i) component presentation phenol: along which it passes -- 0.5-% of the weight bisphenol A: -- amount of : 90-% of the weight or more (ii) extractions:, such as a polyphenol quantity boiling point object of 5.5-% of the weight others, -- the concentration mother liquor passing through Rhine 81 -- receiving -- (9) 17.0-% of the weight strong acid mold ion exchange resin -- a column (R)

(i) -- temperature: -- 53-degree-C (ii) pressure: -- product phenol: passing through 760-torr (10) Rhine 92 -- 89.5-% of the weight bisphenol A: -- 8.0 % of the weight -- in addition to this -- impurity: 2.5-% of the weight (ii) hue APHA: -- 70 [0056] or less

[Effect of the Invention] According to this invention, while preventing are recording of the by-product in the system of reaction, or an impurity, loss of an active principle can be controlled and good bisphenol A of a hue can be manufactured efficiently and economically as crystal adduct with a phenol by the high grade. Moreover, according to the purification approach of the mother liquor separated from the crystallization product by this invention, those high boiling point objects and reactant impurities are economically [ efficiently and ] removable from the mother liquor containing reactant impurities, such as an object which is easy to produce high boiling point objects, such as a sulfonation object of the catalyst origin, a coloring impurity, and coloring, as high-boiling point tarry material. The cyclic use of waste water of the purification mother liquor processed by this invention can be carried out in favor of the reaction process of

an acetone and a phenol including a phenol and bisphenol A. And are recording of the by-product in the system of reaction or an impurity can be prevented by carrying out the cyclic use of waste water of such a purification mother liquor.

---

: [Translation done.]

\* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

TECHNICAL FIELD

---

[Industrial Application] This invention relates to the art of the mother liquor separated from the crystallization product of the phenol solution containing the manufacture approach of bisphenol A, and bisphenol A.

---

[Translation done.]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. \*\*\*\* shows the word which can not be translated.

3. In the drawings, any words are not translated.

---

EFFECT OF THE INVENTION

---

[Effect of the Invention] According to this invention, while preventing are recording of the by-product in the system of reaction, or an impurity, loss of an active principle can be controlled and good bisphenol A of a hue can be manufactured efficiently and economically as crystal adduct with a phenol by the high grade. Moreover, according to the purification approach of the mother liquor separated from the crystallization product by this invention, those high boiling point objects and reactant impurities are economically [ efficiently and ] removable from the mother liquor containing reactant impurities, such as an object which is easy to produce high boiling point objects, such as a sulfonation object of the catalyst origin, a coloring impurity, and coloring, as high-boiling point tarry material. The cyclic use of waste water of the purification mother liquor processed by this invention can be carried out in favor of the reaction process of an acetone and a phenol including a phenol and bisphenol A. And are recording of the by-product in the system of reaction or an impurity can be prevented by carrying out the cyclic use of waste water of such a purification mother liquor.

---

[Translation done.]

## \* NOTICES \*

JPO and NCIP1 are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

 TECHNICAL PROBLEM
 

---

[Description of the Prior Art] In order to manufacture bisphenol A [2 and 2-screw (4'-hydroxyphenyl) propane], the thing [ bottom / of existence of an acid catalyst ] which you react and is made for an acetone to react to a superfluous phenol is known. Moreover, in order to carry out separation recovery of high grade bisphenol A from this resultant, crystallization of the resultant is carried out, the crystal adduct (only henceforth crystal adduct) of bisphenol A and a phenol is deposited, and removing a phenol from the obtained crystal adduct is also known (JP,36-23335,B, JP,52-42790,B). Furthermore, carrying out the cyclic use of waste water of the mother liquor (phenol solution) after separating the crystal adduct obtained with said crystallizing process to a reaction process is also known.

[0003] By the way, it is in the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A, 2-(2'-hydroxyphenyl)-2 which is the isomer of little bisphenol A besides a lot of phenols and bisphenol A -(4'-hydroxyphenyl)-. The coloring impurity and coloring nature impurity of \*\*\*\* small quantity are further contained including by-products, such as bisphenol compounds, such as a propane (only henceforth 2 and 4'-bisphenol A), a tris phenol, a polyphenol compound of the amount of macromolecules, and a chroman compound. And since this mother liquor contains that colored impurity and impurity which is easy to color, it serves as a colored liquid which gives high coloring concentration with heating. Although the reuse of it is circulated through and carried out to the system of reaction since such a mother liquor contains bisphenol A which is the phenol and the specified substance used as the reaction raw material of bisphenol A, when it circulates as it is, since are recording of said by-product, and a coloring impurity and a coloring nature impurity takes place, it is necessary to perform removal of those by-products and impurities. For this reason, it faces carrying out the cyclic use of waste water of the mother liquor to the system of reaction, some mother liquors [ at least ] are contacted to the adsorbent which consists of acid type cation exchange resin, and the approach (JP,55-34779,B) of carrying out adsorption treatment of the coloring object, and circulating through it to the system of reaction after that is learned. However, by this approach, since adsorption treatment of some impurities in a mother liquor is only carried out, in a circulation mother liquor, the by-product or impurity of a considerable amount cannot still remain, and that are recording cannot be prevented.

[0004] According to JP,1-230538,A, the resultant which a phenol and an acetone are made to react and is acquired is carried out the 1st \*\*\*\*, the 1st crystal adduct and the 1st mother liquor are obtained from the obtained 1st crystallization product, and a phenol is removed from the 1st crystal adduct. An isopropenyl phenol and a phenol are mixed with a series of primary routing which obtains bisphenol A to said 1st mother liquor. Carry out the resultant which is made to react under existence of an acid catalyst and is acquired the 2nd \*\*\*\*, and the 2nd crystal adduct and the 2nd mother liquor are obtained from the obtained 2nd crystallization product. The 2nd crystal adduct circulates through this to said 1st crystallizing process. On the other hand, the 2nd mother liquor After making with the resultant which carries out reaction processing of this under existence of a basic catalyst, and contains an isopropenyl phenol and a phenol, the manufacture approach of bisphenol A which consists of a series of subprocesses which carry out the cyclic use of waste water as said isopropenyl phenol and a phenol is

proposed. Since this approach does not circulate through the mother liquor obtained by carrying out crystallization of the resultant of a phenol and an acetone to the system of reaction of a phenol and an acetone using a subprocess, there is an advantage that are recording of a by-product or an impurity does not take place to the system of reaction, but in a subprocess, since are recording of by-products other than polyphenol or an impurity takes place, the purity of the 2nd crystal adduct obtained at a subprocess will become bad. Moreover, if it is going to raise the purity of the 2nd crystal adduct, it is necessary to make a part of 2nd mother liquor from a subprocess discharge out of a system but, and in this case, since bisphenol A, and a phenol and polyphenol are contained, there is a problem that loss of these useful components takes place in that mother liquor.

---

[Translation done.]

## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

MEANS

---

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. According to this invention, the resultant acquired from the reaction process which makes an acetone and the phenol of an excessive amount react under existence of an acid catalyst, and makes bisphenol A generate, and this reaction process Namely, an acetone, The separation process divided into water, a phenol, and the phenol solution containing bisphenol A, The crystallizing process which deposits the crystal adduct of bisphenol A and a phenol from the phenol solution containing this bisphenol A, In the manufacture approach of bisphenol A which consists of a circulation process which circulates the mother liquor obtained at the crystallization product separation process and this crystallization product separation process of separating crystal adduct and a mother liquor from the crystallization product obtained with this crystallizing process to said reaction process (i) The distillation process which obtains the distillate which is made to distill 50 - 90% of the weight of the mother liquor which introduced these some circulation mother liquors [ at least ] into the distilling column, and was introduced into this distilling column, and contains a phenol, (ii) Reduced pressure evaporation of the product obtained at the heating process which heats the bottom of the distilling column obtained with this distillation process (i) at 200-350 degrees C under existence of a basic catalyst, and this (iii) heating process (ii) is carried out. The reduced pressure recovery process of obtaining the distillate steam containing a phenol and an isopropenyl phenol, (iv) The quenching process which the distillate steam obtained at this reduced pressure recovery process (iii) is contacted to the distillate obtained with the distillation process (i), and quenches it, (v) The manufacture approach of bisphenol A characterized by including the circulation process which circulates through the quenching object obtained at this quenching process (iv) at a reaction process is offered.

[0007] Moreover, it faces processing the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A according to this invention. (i) The distillation process which obtains the distillate which is made to distill 50 - 90% of the weight of the mother liquor which introduced these some mother liquors [ at least ] into the distilling column, and was introduced into this distilling column, and contains a phenol, (ii) Reduced pressure evaporation of the product obtained at the heating process which heats the bottom of the distilling column obtained with this distillation process (i) at 200-350 degrees C under existence of a basic catalyst, and this (iii) heating process (ii) is carried out. The reduced pressure recovery process of obtaining the distillate steam containing a phenol and an isopropenyl phenol, (iv) The art of the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A characterized by including the quenching process which the distillate steam obtained at this reduced pressure recovery process (iii) is contacted to the distillate obtained with the distillation process (i), and quenches it is offered.

[0008] Next, this invention is explained, referring to a drawing. Drawing 1 is process drawing for manufacturing bisphenol A by this invention. drawing 1 -- setting -- 1 -- a reaction process and 2 -- a separation process and 3 -- a crystallizing process and 4 -- a crystallization product separation process and 5 -- a distillation process and 6 -- a heating process and 7 -- a reduced



pressure recovery process and 8 -- strong acid mold ion-exchange-resin down stream processing -- each \*\*\*\*.

[0009] In the reaction process 1, the reaction of an acetone and the phenol of an excessive amount is performed under existence of an acid catalyst, and, thereby, bisphenol A is generated. Although mineral acids, such as a hydrochloric acid and a sulfuric acid, and the strong acid mold ion exchange resin which has a sulfonic group are used as an acid catalyst, use of strong acid mold ion exchange resin is desirable. The 8-20 mols of the amount of the phenol used are 10-18 mols in rate preferably to one mol of acetones. Reaction temperature is 50-90 degrees C. The resultant acquired at this reaction process 1 contains a coloring impurity and a coloring nature impurity further including by-products, such as bisphenol compounds, such as 2 which is the isomer of bisphenol A besides bisphenol A which is the specified substance, and 4'-bisphenol A, a tris phenolic compound, a polyphenol compound of the amount of macromolecules, a chroman compound, and water. if the typical presentation of this resultant is shown -- unreacted phenol:60-90wt% -- desirable -- 70 - 80wt% and unreacted acetone:0.1-2wt% -- desirable -- 0.5 - 1.5wt% and bisphenol A:15 - 30wt% -- desirable -- 18 - 25wt% and water:0.1 - 2wt% -- desirable -- 0.5 - 1.5wt% and byproduction polyphenol compound:2 - 15wt% -- it is 5 - 10wt% preferably. This resultant is introduced through Rhine 11 to the separation process 2.

[0010] The separation process 2 is a process which carries out separation processing of the resultant acquired at the reaction process 1, and is mainly divided into the phenol solution containing an acetone, water, a phenol, and bisphenol A, respectively. It circulates through the acetone separated at this separation process 2 at the reaction process 1 through Rhine 12, water is discharged through Rhine 13, a phenol is introduced into the crystallization product separation process 4 as a phenol for washing through Rhine 14, and the phenol solution containing bisphenol A is introduced into a crystallizing process 3 through Rhine 15. If the separation process 2 usually consists of distillation down stream processing including two or more distilling columns, and it is constituted so that it may separate into the specific component which described the resultant above, the separation process of arbitration can be used for it. The distillation processing schematic diagram of the resultant preferably adopted as drawing 2 as a separation process 2 of this invention is shown. drawing 2 -- setting -- 31 -- in the 1st distilling column and 32, the 4th distilling column and 35 show 36 and, as for the 2nd distilling column and 33, a strong acid mold ion-exchange-resin processor and 37 show a settler, as for the 3rd distilling column and 34.

[0011] The resultant acquired at the reaction process 1 which performs the reaction of a phenol and an acetone lets Rhine 38 pass, is introduced into the 1st distilling column 31 which constitutes the 1st distillation down stream processing, and is divided into the bottom material (I) containing an unreacted phenol, bisphenol A, and a by-product, and the overhead product (I) containing an unreacted phenol, an unreacted acetone, and water in this 1st distilling column 31.

[0012] if the component presentation of the overhead product (I) from the 1st distilling column is shown -- phenol:60 - 90wt% -- desirable -- 80 - 90wt% and acetone:2 - 20wt% -- desirable -- 5 - 10wt% and water:5 - 20wt% -- it is 5 - 10wt% preferably. if the component presentation of the bottom material (I) from the 1st distilling column is shown on the other hand -- phenol:50 - 80wt% -- desirable -- 65 - 75wt% and bisphenol A:18 - 30wt% -- desirable -- 20 - 25wt% and by-product:5 - 20wt% -- it is 5 - 10wt% preferably.

[0013] The overhead product (I) obtained in said 1st distilling column is introduced into the 2nd distilling column 32 which constitutes the 2nd distillation down stream processing through Rhine 40, and on the other hand, the bottom material (I) obtained in said 1st distilling column 31 and (the phenol solution containing bisphenol A) are extracted through Rhine 39, and are sent to a crystallizing process 3 through Rhine 15 of drawing 1 as a raw material for crystallization.

[0014] In the 2nd distilling column 32, distillation processing is performed under existence of an oily entrainer, and the overhead product (II) which consists of an acetone, water, and an entrainer is obtained. the component presentation of this overhead product (II) -- acetone:2 - 20wt% -- desirable -- 5 - 20wt% and water:10 - 30wt% -- desirable -- 15 - 25wt% -- it is -- entrainer:40 - 80wt% -- it is 50 - 70wt% preferably. A phenol is obtained from a bottom as a bottom material (II). the content of the acetone in the bottom material (II) of the 2nd distilling

column 32 -- less than [ 5wt% ] -- it is zero % preferably. An entrainer adjusts the service condition of the 2nd distilling column, and it is desirable small quantity and to make 5 or less % of the weight exist at 1 or less % of the weight of a rate especially preferably in the bottom material of the 2nd distilling column. Thereby, the amount of phenol mixing to an overhead product can be reduced.

[0015] The overhead product (II) from the overhead of the 2nd distilling column 32 is introduced into the settler 36 which constitutes a standing process through Rhine 42, and is divided into the oily component which consists of an acetone and an entrainer here, and the aqueous component which consists of an acetone and water. An aqueous component is introduced into the 3rd distilling column 33 for the oily component separated by this settler 36 through Rhine 45 through Rhine 44, respectively. By dividing the overhead product (II) of the 2nd distilling column 32 into an oily component and an aqueous component by the settler 36, the overhead product (II) can be stably supplied to the 3rd distillation process. However, installation of this settler 36 is not necessarily needed, but an overhead product (II) can also supply the 3rd distilling column directly through Rhine 42. On the other hand, the bottom material (II) which consists of a phenol from the 2nd distilling column 32 passes along Rhine 41, and is introduced into the 4th distilling column 34 which constitutes the 4th distillation down stream processing through the strong acid mold ion-exchange-resin processor 35 if needed.

[0016] As an oily entrainer, 80-140 degrees C of 100-140-degree C hydrocarbon oils are preferably used for a boiling range. Toluene, ethylbenzene, a xylene, etc. are mentioned as an example of an entrainer. this entrainer -- the initial complement for [ said ] circulating through the 32nd distilling column 2 and the 3rd distilling column 33 from Rhine 43 on the occasion of the start up of the 2nd distilling column 32, as carried out -- the outside of a system -- a column -- after being supplied inside and dissociating by the settler 37 after a start up, it is returned to the 2nd distilling column 32 through Rhine 43.

[0017] In the 3rd distilling column 33 which constitutes the 3rd distillation down stream processing, an acetone is obtained as an overhead product (III), and this thing is extracted through Rhine 46 and it circulates through it at the reaction process 1 through Rhine 12 shown in drawing 1. the water content in this circulation acetone -- less than [ 5wt% ] -- it is less than [ 3wt% ] preferably. On the other hand, although the bottom material (III) which consists of water and an entrainer is obtained from the bottom of the 3rd distilling column 33, this thing is introduced into the settler 37 which constitutes a standing process through Rhine 47, and is divided into an entrainer and water here. It circulates through an entrainer to the 2nd distilling column 32 through Rhine 43. On the other hand, water is discharged through Rhine 48. the acetone content contained during this wastewater -- less than [ 5wt% ] -- it is zero % preferably.

[0018] In the strong acid mold ion-exchange-resin processor 35, the strong acid mold ion exchange resin serves as a catalyst, and the coloring impurity contained in a bottom material (II) (phenol) and condensation nature impurities, such as a coloring impurity precursor, carry out a condensation reaction, and are changed into a tar-like high boiling point object. In this case, benzofuran etc. is mentioned as a condensation nature impurity. As strong acid mold ion exchange resin, the thing of a gel mold which has a sulfone radical is used, and such strong acid mold ion exchange resin is known well conventionally. For example, Amberlite and Amberlyst which may come to hand from Iom and HASU, the diamond ion which may come to hand from Mitsubishi Kasei Corp. can be used preferably. Processing of the bottom material (II) using this strong acid mold ion exchange resin can be carried out by the approach of circulating the packed column which contains strong acid mold ion exchange resin for a bottom material (II), the approach of putting in and agitating a bottom material (II) to the mixing vessel into which strong acid mold ion exchange resin was put, etc. processing temperature -- 45-150 -- it is 50-100 degrees C preferably. The contact time of strong acid mold ion exchange resin and a bottom material (II) is about 15 - 60 minutes preferably for 5 to 200 minutes. If moisture mixes into a bottom material (II) when processing a bottom material (II) using this strong acid mold ion exchange resin, the impurity removal effectiveness by strong acid mold ion exchange resin will fall. In this distillation approach, as mentioned above, in the 2nd distilling column 32, water is

separated nearly completely as an overhead product component, and since water is not contained on parenchyma in the phenol obtained as a bottom material (II), strong acid mold ion-exchange-resin processing of that bottom material (II) is carried out smoothly.

[0019] If needed, it can mix with the bottom material (II) which lets Rhine 49 pass for a non-refined phenol, and passes along Rhine 41 in the strong acid mold ion-exchange-resin processor 35, and can introduce into it. An industrial use phenol, a mother liquor phenol, a washing waste fluid phenol which were obtained with the crystallizing process, etc. are mentioned to a non-refined phenol.

[0020] The processing product obtained with the strong acid mold ion-exchange-resin processor 35 is introduced into the 4th distilling column 34 through Rhine 50, and is divided into the overhead product (IV) which consists of a phenol here, and the bottom material (IV) which consists of tar-like high-boiling point matter. The service condition of this distilling column requires that a phenol and high-boiling point matter should be completely separable conditions, and it is necessary to perform it on the conditions which the high-boiling point matter does not mix into a phenol. The point with which it should mind in this case is making distillation processing temperature into 190 degrees C or less. Although an operating pressure will be set as arbitration if it is 190 degrees C or less in temperature, reduced pressure thru/or ordinary pressure of 50Torr(s) - 760Torr is usually adopted. Since disassembly of the high-boiling point matter etc. will become remarkable and the quality of a distillate phenol will be reduced if an operating temperature surpasses 190 degrees C, it is not desirable. the phenol introduced in this 4th distilling column 34 -- 99 % of the weight or more is distilled preferably 95% of the weight or more. The hue of the phenol obtained from the overhead of the 4th distilling column 34 is good, and the hue APHA is ten or less. This purification phenol is extracted through Rhine 52, and that part is introduced into the crystallization product separation process 4 through Rhine 14 shown in drawing 1 , and is used as a penetrant remover of the crystal adduct for obtaining high grade bisphenol A. [ at least ] Moreover, the cyclic use of waste water of this purification phenol can also be carried out to the reaction process 1 if needed. The bottom material (IV) extracted through Rhine 51 from the pars basilaris ossis occipitalis of the 4th distilling column 34 usually consists of mixture containing phenol:10-90 % of the weight and high-boiling point matter:10-60 % of the weight. Since the amount of this bottom material (IV) is little, it can be made to discharge out of a system as it is.

[0021] According to the separation process of the resultant shown in drawing 2 , since distillation in the 2nd distilling column 32 is performed under existence of an entrainer, the substantial whole quantity of water and an acetone is separable as an overhead product (II). And this overhead product (II) can be made to divide into water and an acetone nearly completely in the 3rd distilling column 33. That is, the substantial whole quantity of the acetone supplied to the 3rd distilling column 33 can be separated as an overhead product (III) of the 3rd distilling column, and there is no mixing of a parenchyma top acetone in the bottom material (III) of the 3rd distilling column 33. Consequently, there is no mixing of an acetone in wastewater extracted from a settler 37, and the problem of troublesome waste water treatment that an acetone is removed from that wastewater is solved. Moreover, also in the acetone separated from the 3rd distilling column 33 as an overhead product (III), since it is not mixed, reuse of an acetone is also easy for most water.

[0022] Other distillation processing schematic diagrams employable as drawing 3 as a separation process 2 of this invention are shown. In drawing 3 , in 31, the 3rd distilling column and 34 show the 4th distilling column, and, as for the 1st distilling column and 32, 35 shows a strong acid mold ion-exchange-resin processor, as for the 2nd distilling column and 33.

[0023] The product obtained at the reaction process 1 which performs the reaction of a phenol and an acetone lets Rhine 38 pass, is introduced into the 1st distilling column 31 which constitutes the 1st distillation down stream processing, and is divided into the bottom material (I) which contains an unreacted phenol, bisphenol A, and a by-product here, and the overhead product (I) containing an unreacted phenol, an unreacted acetone, and water. the 1st distilling column 31 -- the phenol content in the overhead product (I) -- less than [ 40wt% ] -- it is operated so that it may become the range not more than 30wt% preferably. Thereby, the water

content in \*\*\*\*\* (II) obtained from the 2nd distilling column 32 can be controlled a 5wt% less or equal, especially less than [ 2wt% ]. if the component presentation of the overhead product (I) of the 1st distilling column 31 is shown -- less than [ phenol:40wt% ] -- desirable -- less than [ 30wt% ] and acetone:20 - 45wt% -- desirable -- 30 - 40wt% and water:20 - 45wt% -- it is 30 - 40wt% preferably. if the component presentation of the bottom material (I) of the 1st distilling column 31 is shown on the other hand -- phenol:55 - 80wt% -- desirable -- 65 - 75wt% and bisphenol A:18 - 30wt% -- desirable -- 20 - 25wt% and by-product:5 - 15wt% -- it is 6 - 10wt% preferably. The overhead product (I) obtained in said 1st distilling column 31 is introduced into the 2nd distilling column 32 which constitutes the 2nd distillation down stream processing through Rhine 40, and, on the other hand, the bottom material (I) obtained in said 1st distilling column 31 is introduced into the 4th distilling column 34 through Rhine 39.

[0024] In the 2nd distilling column 32, an acetone is obtained as an overhead product (II), and this thing is extracted through Rhine 46 and it circulates through it at the reaction process 1 through Rhine 12 shown in drawing 1. the water content in this circulation acetone -- less than [ 10wt% ] -- it is less than [ 5wt% ] preferably. On the other hand, the bottom material (II) which consists of mixture of a phenol and water is obtained from the bottom of the 2nd distilling column 32, and this thing is introduced into the 3rd distilling column 33 through Rhine 47. the component presentation of the bottom material (II) of the 2nd distilling column 32 -- phenol:40 - 60wt% -- desirable -- 40 - 50wt% and water:40 - 60wt% -- it is 50 - 60wt% preferably, and the content of an acetone is less than [ 1wt% ].

[0025] In the 3rd distilling column 33 which constitutes the 3rd distillation down stream processing, water is obtained as an overhead product (III) and this thing is discharged through Rhine 48. On the other hand, although the bottom material (III) which consists of a phenol is obtained from the bottom of the 3rd distilling column 33, after this thing is processed with the strong acid mold ion-exchange-resin processor 35 through Rhine 41, it is introduced into the 4th distilling column 34 which constitutes the 4th distillation down stream processing. Moreover, if needed, to the bottom material (III) of this 3rd distilling column 33, it can add through Rhine 49, and a non-refined phenol can be introduced into the strong acid mold ion-exchange-resin processor 35 at it. In this case, as a non-refined phenol, an industrial use phenol, a mother liquor phenol, a washing waste fluid phenol which are obtained with a crystallizing process, etc. are mentioned.

[0026] In the strong acid mold ion-exchange-resin processor 35, the strong acid mold ion exchange resin serves as a catalyst, and condensation nature impurities contained in a phenol, such as a coloring impurity and a coloring impurity precursor, carry out a condensation reaction, and are changed into a tar-like high boiling point object. The processing product obtained with the strong acid mold ion-exchange-resin processor 35 is introduced into the 4th distilling column 34 which constitutes the 4th distillation down stream processing through Rhine 50, and a phenol is acquired as an overhead product (IV) here. Moreover, the bottom material (I) and (the phenol solution containing a bisphenol) of the 1st distilling column 31 are introduced into this 4th distilling column 34 through Rhine 39. In this 4th distilling column 34, although a phenol is distilled from that overhead, the hue of this phenol is good and that hue APHA is ten or less. As this purification phenol is shown in drawing 1, it circulates at least through that part at the crystallization product separation process 4 through Rhine 14, and it is used as a penetrant remover of the crystal adduct for obtaining high grade bisphenol A. Moreover, the cyclic use of waste water of this purification phenol can be carried out to the reaction process 1 if needed. The bottom material (IV) extracted through Rhine 51 from the pars basilaris ossis occipitalis of the 4th distilling column 34 usually, a bisphenol -- 15 - 30wt% -- preferably Including 20 - 25wt%, preferably, including a phenol 50 to 80% of the weight, 65 to 75% of the weight, a by-product is further included at 6 - 10% of the weight of a rate preferably five to 15% of the weight, and as shown in drawing 1, it is introduced as a raw material for crystallization through Rhine 15 to a crystallizing process 3. In addition, the bottom material (I) of the 1st distilling column 31 can also be introduced to a crystallizing process 3 as it is, without introducing into the 4th distilling column 34.

[0027] According to the separation process of the resultant shown in drawing 3, by holding the

phenol content in the overhead product (I) obtained from the 1st distilling column 31 to 40 or less % of the weight, the substantial whole quantity of the acetone supplied to the 2nd distilling column 32 can be separated as an overhead product (II) of the 2nd distilling column, and there is no mixing of a parenchyma top acetone in the bottom material (II) of the 2nd distilling column 2. Consequently, in the 3rd distilling column 33, there is no mixing of an acetone in the water separated as that overhead product (III), and the problem of troublesome waste water treatment that an acetone is removed from that sejunction water is solved. Moreover, according to this separation process, in the 3rd distilling column, since an acetone does not exist, that distillation actuation can be performed efficiently.

[0028] A crystallizing process 3 is a process which the solution containing bisphenol A obtained at the separation process 2 as was the above is cooled [ process ], and deposits the crystal adduct of bisphenol A and a phenol. In this case, 35-80 degrees C of crystallization temperature are 45-70 degrees C preferably. The crystallization product (crystal adduct slurry) obtained with this crystallizing process is introduced into the crystallization product separation process 4 through Rhine 16 in drawing 1 . Although a crystallizing process 3 can consist of one or more crystallization phases, it shows the crystallization schematic diagram about one example of the crystallizing process to drawing 4 . drawing 4 -- setting -- 55 -- an outer case and 56 -- a container liner and 57 -- a microcrystal adduct solution tank and 58 -- a condensator and 59 -- a heater, and 60 and 61 -- a pump and A -- crystallization -- a column is shown. crystallization -- a column -- A has the double cylinder structure which inserted the container liner 56 which has opening in the upper part into the outer case 55 of sealing structure. the sealing structure as used in this specification -- crystallization -- a column is not in an atmospheric-air disconnection condition, but the condition that the seal is carried out in inert gas is said. crystallization -- a column -- A is atmospheric-air disconnection -- crystallization -- a column -- while a part of oxygen in atmospheric air is absorbed by the inner slurry and worsening the hue of adduct, in latter processing, it has a bad influence, and it becomes impossible for adduct \*\*\*\*\* of high quality to obtain bisphenol A of high quality further therefore, crystallization -- a column -- in A, in order to prevent mixing of oxygen, it will be necessary to carry out a seal in inert gas In this case, if mixing of oxygen can be prevented, it is not necessary to be necessarily the sealing proof-pressure container which can bear high pressure. moreover, crystallization -- a column -- in A, after preparing a container liner on the medial axis of the revolution style of an internal slurry rather than preparing a direct extraction hole in the outer case section, raising the revolution style of a slurry to the upper part, carrying out overflow of the slurry from opening of the container liner upper part and dropping the interior of a container liner, it is good to take the approach of extracting from a container liner pars basilaris ossis occipitalis. Thereby, sufficient residence time is securable to an adduct particle with uniform mixing to the introduced circulation slurry.

[0029] In order to carry out a crystallizing process according to the crystallization schematic diagram shown in drawing 4 first, some phenol solutions containing bisphenol A which is the processed raw material extracted through Rhine 15 of drawing 1 from the separation process 2 -- Rhine 62 and Rhine 63 -- passing -- crystallization -- a column, while being filled up in A the pars basilaris ossis occipitalis of a container liner 56 to Rhine 64 -- passing -- a phenol solution -- an extract and this -- Rhine 65, a pump 60, Rhine 66, a condensator 58, Rhine 67, and Rhine 63 -- letting it pass -- crystallization -- a column -- it is made to circulate continuously in the outer case of A lower part this actuation -- crystallization -- a column -- it is cooled, crystal adduct carries out crystallization of the phenol solution in A, and the slurry containing crystal adduct is generated. the crystallization as it was the above, after this slurry was extracted from the pars basilaris ossis occipitalis of a container liner 56, and being cooled with the condensator 58 -- a column -- it comes to circulate in the outer case 55 of A lower part. moreover, the pars basilaris ossis occipitalis of a container liner 56 to a part of slurry -- Rhine 64, Rhine 68, a pump 61, Rhine 69, a heater 59, a tank 57, and Rhine 70 and 71 -- passing -- crystallization -- a column -- it is made to circulate continuously in the outer case 55 of A lower part by this actuation, the microcrystal adduct particle in the slurry extracted from the pars basilaris ossis occipitalis of a container liner 56 dissolves by the tank 57 -- having -- a slurry with low

microcrystal adduct particle content -- crystallization -- a column -- it circulates in A. consequently, crystallization -- a column -- the content of the microcrystal adduct particle in A comes to decrease.

[0030] next, the phenol solution which contains bisphenol A extracted through Rhine 15 from the separation process 2 in such a condition -- Rhine 62 and Rhine 63 -- letting it pass -- crystallization -- a column -- while introducing in the outer case 55 of A lower part, a product slurry is extracted through Rhine 73 from the pars basilaris ossis occipitalis of a container liner 56. In this case, when this slurry can be passed by the gravity flow to the following crystallization product separation process, it extracts using Rhine 73 in this way, but when that is not right, that part can also be extracted from regurgitation Rhine 74 of a pump 61. Moreover, a part of slurries with little microcrystal content can be collected from Rhine 72, and this can also be made into a product crystal adduct slurry. These crystal adduct slurries can perform the still more nearly same crystallization processing as the above if needed.

[0031] The slurry passing through the slurry passing through Rhine 63 which carried out the temperature reduction, and Rhine 70 and 71 which carried out the temperature rise is faced making it introduce in an outer case 55, and is better than the outer case lower part in an outer case to introduce so that the revolution style of the same sense may be produced. In this case, preferably, it introduces so that it may become a tangential direction to outer case inner skin, and it carries out so that those introductory locations may differ. if an introductory location is too near -- the turbulence of local flow -- being generated -- a smooth revolution style -- it cannot obtain -- becoming -- moreover, crystallization -- it is not desirable from the structure of a column, and a strong field. Therefore, the introductory location of these two slurries is good to carry out in the location which expressed with the include angle and was preferably separated from the central point of an outer case 90 to 180 degrees. Furthermore, if it is for the revolution style of the same sense to arise, the introductory location of two slurries does not necessarily need to be on the same horizontal plane, and even if there is a difference of some height, it will not interfere in the outer case lower part at least. As it is the above, if each slurry passing through Rhine 63 and Rhine 70 and 71 is introduced so that the revolution style of the same sense may be produced in an outer case, this revolution style will go up the inside of an outer case 55 to the upper limit section of a container liner 56, and will descend the inside of a container liner 56 from up opening of a container liner 56, and will be extracted through Rhine 64 from the pars basilaris ossis occipitalis of that container liner. The following effectiveness can be acquired by producing such a revolution style in an outer case 55.

- (1) Two liquid flows of different temperature are effectively mixable to homogeneity.
- (2) Since channeling of a slurry is prevented and the slurry concentration in an outer case becomes homogeneity, the nonuniformity of the residence time within the outer case of a crystal adduct particle can be lost.
- (3) Sufficient linear velocity which is sufficient for preventing sedimentation deposition within the outer case of a crystal adduct particle can be obtained.

[0032] Moreover, a part of slurry extracted from container liner 56 pars basilaris ossis occipitalis as mentioned above Rhine 64, Rhine 68, a pump 61, a heater 59, a tank 57, and Rhine 70 and 71 -- letting it pass -- crystallization -- a column, when circulating A From dissolution disappearance of the microcrystal adduct in a slurry being carried out within a tank 57 It circulates to A. the slurry containing the big and rough crystal adduct of fixed magnitude -- Rhine 70 and 71 -- passing -- crystallization -- a column -- this -- crystallization -- a column -- the particle size of the crystal adduct contained in A arranges -- having -- crystallization -- a column -- in A, microcrystal adduct particle content is low and the high crystal adduct of big and rough crystal adduct particle content is generated. crystallization -- a column -- since the specific surface area is large, the microcrystal adduct in A shows adsorbent [ high ] to a coloring causative agent. therefore, crystallization -- a column -- the good crystal adduct of a hue can be obtained by decreasing the microcrystal adduct particle content in the crystal adduct obtained by A as much as possible. The good high grade crystal adduct of a hue can be manufactured by holding preferably microcrystal adduct particle content with a particle size [ in crystal adduct ] of 100 micrometers or less to 20 or less % of the weight 30 or less % of the

weight.

[0033] temperature with the temperature of the phenol solution containing bisphenol A supplied from Rhine 62 higher about 1-20 degrees C than the saturation temperature of crystal adduct -- it is -- crystallization -- a column -- the temperature of A is 45-70 degrees C. In a condensator 58, 5-degree-C or less extent descent of about 10 degrees C or less of the slurries which circulate through Rhine 65, a pump 60, a condensator 58, and Rhine 63 is preferably carried out in the temperature. crystallization -- a column -- the residence time of the phenol solution in A is 0.5 - 5 hours preferably for 0.5 to 10 hours. On the other hand, in the heater 59, the slurry introduced into the microcrystal adduct solution tank 57 through Rhine 68, a pump 61, Rhine 69, and a heater 59 goes up the temperature by about 0.5-5 degrees C, and is held at the microcrystal solution tank 57. The residence time of the phenol solution in this tank 57 is about 3 - 15 minutes.

[0034] Crystal adduct with a particle size of 100 micrometers or less is dissolved into the microcrystal solution tank 57. Crystal adduct particle content with a particle size [ in the crystal adduct in the slurry passing through Rhine 70 ] of 100 micrometers or less is 20 or less % of the weight preferably 30 or less % of the weight.

[0035] According to said crystallization method, the good crystal adduct of a hue with low microcrystal adduct particle content can be made to generate efficiently. This crystal adduct gives good bisphenol A of a hue by from now on carrying out separation removal of the phenol.

[0036] The crystal adduct slurry (crystallization product) obtained with said crystallizing process 3 is sent to the crystallization product separation process 4. In this crystallization product separation process 4, a crystal adduct slurry is divided into crystal adduct and a mother liquor, and washing processing of the crystal adduct is carried out, using the purification phenol extracted through Rhine 14 from the separation process 2 as a penetrant remover. And if needed, with a phenol [ finishing / washing ], the separated mother liquor is extracted from the crystallization product separation process 4 through Rhine 17, and it circulates through it at the reaction process 1. In this case, at least, it introduces into the mother liquor purification process of a circulation mother liquor which usually carries out the postscript of this one to 20% of the weight in part, and processes. And the mother liquor by which purification processing was carried out makes the reaction process 1 circulate through this again.

[0037] In the crystallization product separation process 4, when carrying out filtration processing of the crystal adduct slurry and separating crystal adduct from a mother liquor, it is desirable that make a part of microcrystal adduct component [ at least ] with a particle size of 100 micrometers or less shift to a filtrate (mother liquor) side among the crystal adducts contained in the slurry, and the rate of a microcrystal adduct component with a particle size of 100 micrometers or less obtains 15 or less % of the weight of big and rough crystal adduct preferably 20 or less % of the weight. In this case, in order to make a microcrystal adduct component shift to a filtrate side, selection of a filter (filtering medium) and selection of a filtration operating condition can perform. Generally as a filter, 100-300 micrometers of 150-250-micrometer things are preferably used for the \*\*\*\*. moreover, the crystal adduct from which the amount of shift of the microcrystal adduct component is obtained by the filtration processing when making a microcrystal adduct component shift to a filtrate side according to a filtration operating condition -- the frequency which carries out a back wash can adjust the thickness of a cake, and its cake.

[0038] Although the crystal adduct which is the above, and was made and obtained is a high-definition thing which has a low impurity content in itself, it can raise that grace further by washing this crystal adduct further with the purification phenol extracted through Rhine 14 from the separation process 2. Washing of the crystal adduct by the purification phenol should just be the approach that contact to crystal adduct and a purification phenol may fully be attained. In solid-liquid separators, such as a filter for separating for example, crystal adduct, and a centrifugal separator, this washing processing can also wash the crystal adduct to which the approach of introducing a purification phenol in that solid-liquid separator, and washing it and the little mother liquor discharged from a solid-liquid separator adhere with a purification phenol in another mixing vessel, after removing a mother liquor from crystal adduct. The operating rates of



a purification phenol to crystal adduct are more than the 100 weight sections preferably more than 50 weight sections to the crystal adduct 100 weight section.

[0039] Although the crystal adduct by which washing processing was carried out with the purification phenol is a crystal which consists of an equimolar presentation of bisphenol A and a phenol, this thing can remove a phenol at a direct dephenolation process delivery and here, can collect product bisphenol A of a high grade, and after processing at a crystallizing process and a crystallization product separation process again, it can collect delivery and product bisphenol A of a super-high grade at a dephenolation process. Removal of a phenol can be conventionally performed from crystal adduct by approaches, such as a well-known approach, for example, distillation, an extract, and steam stripping.

[0040] According to the above mentioned filtration of a crystal adduct slurry and washing processing of crystal adduct, the good crystal adduct of the thermal stability which can remove efficiently the adsorbent high impurity of the coloring matter adhering to a crystal adduct front face, the coloring nature matter, etc., and is excellent in a hue by this, and cannot produce coloring easily can be obtained easily. Moreover, it is the high-definition thing which bisphenol A which removes a phenol and is obtained from this crystal adduct is also excellent in a hue, and cannot produce coloring easily.

[0041] Although the cyclic use of waste water of the mother liquor obtained from the crystallization product separation process 4 as was the above is carried out to the reaction process 1 through Rhine 17 and Rhine 19 which were shown in drawing 1, a part of the circulation mother liquor [ at least ] is extracted from Rhine 17, and purification processing is carried out by the (i) distillation process 5, (ii) heating process 6, the reduced pressure recovery process 7, and the strong acid mold ion-exchange-resin down stream processing 8 through Rhine 18. Although the heating process 6 and the reduced pressure recovery process 7 can be carried out independently, respectively, it is desirable to carry out to coincidence using a reactor.

[0042] The processing schematic diagram about one example of the purification art of the mother liquor extracted through drawing 1 Rhine 17 and 18 by drawing 5 is shown. drawing 5 -- setting -- 5 -- a phenol distilling column and D -- a reaction vessel 6 and reduced pressure evaporation -- the reactor and R which have a column 7 -- strong acid mold ion exchange resin -- a column is shown. A raw material mother liquor is introduced into the phenol distilling column 5 through Rhine 18. In this case, as a raw material mother liquor, some mother liquors [ at least ] obtained at the crystallization product separation process 4 can be used. In crystallization processing of the phenol solution containing bisphenol A, although two or more steps of crystallizing processes and the solid-liquid-separation process of a crystallization product are adopted and two or more sorts of mother liquors (phenol solution) are usually obtained according to it, by this invention, the thing of the arbitration of these mother liquors can be used as a raw material mother liquor. The desirable raw material mother liquor used by this invention is a mother liquor separated from the 1st crystallization product obtained with the crystallizing process of the 1st step. The coloring nature impurity which usually changes into the coloring matter the mother liquor separated from this crystallization [ 1st ] product with heating of coloring nature impurity: 2 or less % of the weight aldehydes, such as a chroman compound, a quinone, etc. polyphenol: 1-5% of the weight of others which contain 4[ 2 and ]-bisphenol A fail: 85 % of the weight and bisphenol A: 5-10% of the weight: Contain a minute amount.

[0043] the phenol distilling column 5 -- temperature: -- it is preferably operated by 100-200 degrees C on 120-185-degree-C, pressure: 50 torr - ordinary pressure conditions. In this phenol distilling column 5, the raw material mother liquor introduced from Rhine 18 is desirable 50 to 90% of the weight, and 65 - 85 % of the weight is distilled. If the amount of distillates increases more than this range, it will become hyperviscosity and problems, such as bottom material solidification and the Rhine lock out, will arise, on the other hand, if fewer than this range, the concentration of a phenol will become high and the problem of the processing effectiveness and thermal efficiency in a heating process or a reduced pressure recovery process falling will arise. After the distillate steam from the phenol distilling column 5 is condensed with the condenser 85 attached to this distilling column, that part is returned to a distilling column 5 through Rhine 86



as reflux, and the condensate (distillate) of the remainder is introduced into the reduced pressure condenser 90 attached to Reactor D through Rhine 87. The distillate passing through this Rhine 87 consists of phenol 100% mostly. On the other hand, that bottom is extracted through Rhine 81 from the pars basilaris ossis occipitalis of the phenol distilling column 5, this bottom is introduced into the reaction vessel 6 of the pars basilaris ossis occipitalis of Reactor D through Rhine 84 with the basic catalyst supplied through Rhine 83, and evaporation recovery processing of the concentration mother liquor containing the product generated by this reaction is performed to the reaction and coincidence of the reactant component contained in it here. In addition, supply of a basic catalyst can also be directly performed to the reaction vessel 6 of Reactor D. the bottom extracted through Rhine 81 from the pars basilaris ossis occipitalis of the phenol distilling column 5 -- usually -- phenol: -- ten to 50% of the weight, it is 15 - 30 % of the weight preferably, and the remainder consists of bisphenol A, 2, 4'-bisphenol A, other polyphenol, and other impurities.

[0044] In Reactor D, while the pyrolysis of the polyphenol contained in a concentration mother liquor in the reaction vessel 6, such as a bisphenol and a tris phenol, is carried out by operation of a basic catalyst and it is converted into an isopropenyl phenol and a phenol, the polycondensation reaction of impurities, such as a chroman compound, occurs and an impurity is changed into a high boiling point object. As a basic catalyst, the hydroxide of alkaline earth metal, such as the hydroxide of alkali metal, such as sodium and a potassium, an oxide, a carbonate, various phenol salts, calcium, and magnesium, an oxide, a carbonate, various phenol salts, etc. are mentioned. The operating rate of this basic catalyst is 0.01 - 0.5 % of the weight preferably 0.005 to 0.8% of the weight to all the polyphenol containing bisphenol A in the concentration mother liquor extracted through Rhine 81.

[0045] Reactor D -- a pars basilaris ossis occipitalis -- a reaction vessel 6 -- having -- the reaction-vessel top -- reduced pressure evaporation -- it has the structure which set up the column 7. this reactor D -- bottom (reaction vessel) temperature: 200-350 degree C -- desirable -- 220-300 degrees C and a column -- internal pressure: 5 torr - ordinary pressure -- it is preferably operated on 10-150-torr conditions. Rhine 91 after carrying out mixed contact with the distillate which the distillate steam containing the phenol and isopropenyl phenol which were extracted through Rhine 89 from the crowning of Reactor D was introduced into the reduced pressure condenser 90 attached to Reactor D, and took Rhine 87 from the phenol distilling column 5, and was introduced here and quenching -- passing -- strong acid mold ion exchange resin -- a column -- it is introduced into R. 45-150 degrees C of temperature of the distillate sent to the reduced pressure condenser 90 through Rhine 87 from the phenol distilling column 5 are 50-110 degrees C preferably. moreover, the weight ratio to the distillate steam with which the amount of the distillate passing through Rhine 87 passes along Rhine 89 -- 1-20 -- it is 2-15 preferably. The component of the distillate steam extracted from Reactor D through Rhine 89 is the impurity of a phenol, an isopropenyl phenol, bisphenol A, and others. the liquid with which the bottom (reaction mixture) extracted from Reactor D through Rhine 88 is supplied to Reactor D through Rhine 84 -- receiving -- a weight ratio -- 0.05-0.5 -- it is 0.05-0.4 preferably, and while a high boiling point object (it has the boiling point higher than bisphenol A) is condensed by this bottom, the matter of coloring nature is condensed. the mixed liquor in the reduced pressure condenser 90 -- Rhine 91 -- passing -- strong acid mold ion exchange resin -- a column -- it is introduced into R. this strong acid mold ion exchange resin -- a column -- bisphenol A is generated by the reaction of the isopropenyl phenol and phenol which are contained in mixed liquor in R. The product containing this bisphenol A is discharged through Rhine 92, and is introduced into circulation mother liquor Rhine 19 or the reaction process 1 shown in drawing 1 through Rhine 25.

[0046] As strong acid mold ion exchange resin, the thing of a gel mold which has a sulfone radical is used, and such strong acid mold ion exchange resin is known well conventionally. For example, Amberlite and Amberlyst which may come to hand from Ioam and HASU, the diamond ion which may come to hand from Mitsubishi Kasei Corp. can be used preferably. In the reaction of the mixed liquor using this strong acid mold ion exchange resin, 45-130 degrees C of that reaction temperature are 50-100 degrees C preferably, and contact time is 15 - 120 minutes

preferably for 5 to 200 minutes. When reacting the mixed liquor using this strong acid mold ion exchange resin, the moisture in mixed liquor is preferably carried out to 0.1 or less % of the weight 0.5 or less % of the weight. strong acid mold ion exchange resin -- the component of the resultant extracted through Rhine 92 from Column R -- phenol:85-95 % of the weight and bisphenol A: -- five to 15% of the weight, it is other impurity:minute amounts and coloring nature is preferably low five to 10% of the weight. As shown in drawing 1 , the cyclic use of waste water of this thing is carried out to the reaction process 1 through Rhine 25. Moreover, if needed, concentration crystallization of the part can be carried out, and it can consider as bisphenol A and phenol crystal adduct. in addition, strong acid mold ion exchange resin -- a column -- R is not necessarily needed but the direct reaction process 1 can be made to circulate through the overhead product of the reaction distillation D

[0047] As shown in drawing 6 , as for Reactor D, it is desirable to attach and use a heat treatment equipment A and the stagnation tub B. In operation of such a reactor D, it passes along Rhine 96 from the reaction vessel 6 of the pars basilaris ossis occipitalis of Reactor D, and a part of the bottom material is extracted, and after a part of the extracted bottom material is introduced into a heat treatment equipment A through Rhine 97 as the 1st circulation liquid and it receives heat-treatment here, it circulates to the reaction vessel 6 of Reactor D through Rhine 94 and Rhine 95. In a heat treatment equipment A, the 200-350 degrees C of the 1st circulation liquid are preferably heated by the temperature of 230-300 degrees C under existence of a basic catalyst. With this heating, the polyphenol contained in the 1st circulation liquid undergoes the above mentioned pyrolysis reaction. The residence time of the 1st circulation liquid in a heat treatment equipment A is 1 - 20 minutes preferably for 1 to 30 minutes. On the other hand, a part of bottom material extracted from the pars basilaris ossis occipitalis of the reaction distilling column D circulates to the reaction vessel 6 of Reactor D as the 2nd circulation liquid through Rhine 98, Rhine 99, the stagnation tub B, and Rhine 100. In the stagnation tub B, the 200-300 degrees C of the 2nd circulation liquid are preferably held for 10 - 100 minutes in the temperature of 220-280 degrees C for 5 to 120 minutes. When the depolymerization of the polyphenol contained in a mother liquor is inadequate, while that depolymerization advances further by this stagnation processing, when heavy-izing of a coloring causative agent, for example, a chroman compound, is inadequate, that heavy-ization advances further and the effectiveness of being changed into the easy high-boiling point tarry material of separation is acquired. the concentration mother liquor 100 weight section by which the circulating load of the 1st circulation liquid is supplied to Reactor D through Rhine 100 -- receiving -- the 50 - 5000 weight section -- it is -- on the other hand -- the circulating load of the 2nd circulation liquid -- the same -- the 10 - 10000 weight section -- it is the 50 - 5000 weight section preferably.

[0048] In the art of the above mentioned mother liquor, the impurity contained in a mother liquor lets Rhine 23 ( drawing 1 ) or Rhine 88 ( drawing 5 , drawing 6 ) connected with the bottom or reaction vessel 6 of Reactor D pass, and is discharged as a concentration impurity. The by-product of a high-boiling point and the condensate of a condensation nature impurity are contained rather than bisphenol A, and further, when the ion exchange resin which has the strong acid nature matter of a high-boiling point, for example, a sulfonic group, as a catalyst in the reaction process 1 is used, the sulfonation object isolated from that catalyst is contained in this concentration impurity. Therefore, according to the art of the above mentioned mother liquor, separation removal of each high boiling point object (sulfonation object etc.) of the catalyst origin further used at the reaction process 1 is carried out from a mother liquor in the polyphenol compound contained in the mother liquor, a coloring impurity, a coloring nature impurity, and the condition of having been condensed. And by circulating through the mother liquor from which it did in this way and the by-product and the impurity were removed at the reaction process 1 again, loss of the useful component contained in a mother liquor can be suppressed, and are recording of the by-product in the system of reaction and an impurity can be prevented, consequently bisphenol A which is a high grade and by which coloring was prevented can be obtained.

---

[Translation done.]

## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## EXAMPLE

[Example] Next, an example explains this invention to a detail further.

[0050] (I) -- the reaction process 1 -- according to the well-known approach, the reaction of an acetone and a phenol was conventionally performed under existence of the ion exchange resin which has a sulfonic group. In this case, 14 mols of phenols per one mol of acetones were used. The reaction was performed at 60 degrees C. Thus, the presentation of the acquired resultant was as follows.

Bisphenol A: 0.8wt% water : 1.0wt% phenol : 73.6wt% bisphenol A: 18.8wt% others : 5.8wt% [0050]  
(II-1) Separation process ( drawing 2 )

According to the schematic diagram shown in drawing 2 , distillation processing of the phenol and acetone resultant which were acquired at said reaction process 1 was carried out. In this case, relation with Rhine or equipment shown in drawing 2 shows the used main operating conditions below.

(1) The overhead product passing through Rhine 40 (I)

(i) Component presentation acetone : 5.8wt% phenol : 7.2wt% water : 86.1wt% others : Overhead product passing through 0.9wt% (2) Rhine 42 (II)

(i) Component presentation acetone : 18.5wt% water : 22.5wt% entrainer : 55.6wt% others : Bottom material passing through 3.4wt% (3) Rhine 41 (II)

(i) Component presentation phenol : 99.0wt% entrainer : 0.5wt% others : Overhead product passing through 0.5wt% (4) Rhine 46 (III)

(i) Component presentation acetone : 85.1wt% water : 1.0wt% others : (Wastewater i) component water of constitution passing through 13.9wt% (5) Rhine 48 : 99.95wt% phenol : 0.05wt% [0051] (II-2) Separation process 2 ( drawing 3 )

According to the equipment schematic diagram shown in drawing 3 , the resultant of the phenol and acetone which were obtained at said reaction process 1 was processed. In this case, relation with Rhine or equipment shown in drawing 3 shows the used main operating conditions below.

(1) The overhead product passing through Rhine 40 (I)

(i) Component presentation acetone : 29.0 wt% water : 38.8 wt% phenol : 29.9 wt% others : 2.3 Overhead product passing through wt% (2) Rhine 46 (II)

(i) Component presentation acetone : 89.7 wt% water : 2.1 wt% others : 8.2 Bottom material passing through wt% (3) Rhine 47 (II)

(i) Component water of constitution : 55.5 wt% phenol : 44.2 wt% others : 0.3 Overhead product passing through wt% (4) Rhine 48 (III)

(i) Component water of constitution : 99.7 wt% phenol : 0.2 wt% others : 0.1 Bottom material passing through wt% (5) Rhine 41 (III)

(i) Component presentation phenol : 99.0 wt% others : 1.0 wt% [0053] (III) Crystallizing process 3 ( drawing 4 )

According to the equipment schematic diagram shown in drawing 4 , crystallization processing of the phenol solution containing bisphenol A was carried out, and the slurry (crystallization product) containing crystal adduct was obtained. Relation with Rhine or equipment shown with the sign in drawing 4 shows the main operating conditions in this case below.

(1) component presentation bisphenol A [ of the feed in Rhine 62 ]: -- 22-% of the weight phenol:

-- 74 % of the weight -- in addition to this -- : -- 4-% of the weight -- crystallization -- column A (i) temperature: -- 50-degree-C (ii) residence-time: -- 120-minute (3) crystallization -- a column -- it attached to A -- microcrystal adduct solution tank 57 (i) -- temperature: -- 51-degree-C (ii) residence-time: -- the rate of a particle with a particle size [ in the crystal adduct separated from the slurry obtained through Rhine 73 in said experiment for 6 minutes ] of 100 micrometers or less was 20 % of the weight.

[0054] (IV) -- the crystal adduct obtained after carrying out filtration under reduced pressure with the filter which set the filter cloth which has a 106-micrometer opening for the crystal adduct slurry obtained by carrying out crystallization processing of the phenol solution containing crystallization product separation process 4 bisphenol A, holding slurry temperature at 50 degrees C -- the purification phenol which was able to be obtained from the separation process 2 of the above (II-1) washed the cake. The rate of the microcrystal adduct component 100 micrometers or less in this washing crystal adduct was 5 % of the weight. It was 10APHA(s), and the concentration of a coloring impurity was remarkable and that of the melting color of this crystal adduct was low. Moreover, the concentration of the chroman compound (coloring nature impurity) contained in this crystal adduct was 100wtppm(s).

[0055] (V) Purification processing of the mother liquor separated from the crystallization product ( drawing 5 )

According to the equipment schematic diagram shown in drawing 5 , the mother liquor separated from the crystallization product of the phenol solution containing bisphenol A was processed. In this case, the used main operating conditions are shown below in connection with Rhine or equipment shown in drawing 5 .

(1) (mother liquor i) component presentation phenol: passing through Rhine 18 -- 86.3-% of the weight bisphenol A: -- 7.7 % of the weight 2 and 4'-bisphenol A:2.4 % of the weight -- in addition to this -- an or more [ : 3.6 % of the weight (ii) hue APHA: ] 500(2) phenol distilling column (5) [ , such as a tris phenol, polyphenol, a coloring impurity, and a coloring nature impurity, ]

(i) -- bottom temperature: -- 170-degree-C (ii) pressure : (Distillate i) component presentation phenol: passing through 170-torr (3) Rhine 11 -- bottom material (concentration mother liquor) passing through 99.8-% of the weight or more (ii) hue APHA:10 (4) Rhine 81

(i) -- component presentation phenol: -- 14.8-% of the weight bisphenol A: -- 48.5 % of the weight 2 and 4'-bisphenol A: -- the concentration mother liquor which passes along addition:Rhine 81 of the basic catalyst (NaOH) in or more [ :21.9 % of the weight (ii) hue APHA: ] 500 (5) Rhine 83, such as a tris phenol, polyphenol, a coloring impurity, and a coloring nature impurity, in addition to this 14.8% of the weight -- receiving -- 0.05-% of the weight reaction [ (6) ] \*\*\*\*\* (D)

(i) -- bottom temperature: -- 250-degree-C (ii) pressure : distillate (steamy i) component presentation phenol: passing through 40-torr (7) Rhine 89 -- a 92.6-% of the weight isopropenyl phenol -- and -- in addition to this -- : -- 7.4-% of the weight (ii) hue APHA:200 (8) Rhine 88 (Bottom i) component presentation phenol: along which it passes -- 0.5-% of the weight bisphenol A: -- amount of :90-% of the weight or more (ii) extractions:, such as a polyphenol quantity boiling point object of 5.5-% of the weight others, -- the concentration mother liquor passing through Rhine 81 -- receiving -- (9) 17.0-% of the weight strong acid mold ion exchange resin -- a column (R)

(i) -- temperature: -- 53-degree-C (ii) pressure: -- product phenol: passing through 760-torr (10) Rhine 92 -- 89.5-% of the weight bisphenol A: -- 8.0 % of the weight -- in addition to this -- less than [ impurity:2.5 % of the weight (ii) hue APHA:70 ]

[Translation done.]

## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

DESCRIPTION OF DRAWINGS

---

## [Brief Description of the Drawings]

[Drawing 1] Process drawing for manufacturing bisphenol A by this invention is shown.

[Drawing 2] The distillation processing schematic diagram about one example for dividing the resultant of an acetone and a phenol into a specific component is shown.

[Drawing 3] The distillation processing schematic diagram about other examples for dividing the resultant of an acetone and a phenol into a specific component is shown.

[Drawing 4] The crystallization schematic diagram about one example of the crystallizing process of the phenol solution containing bisphenol A is shown.

[Drawing 5] The processing schematic diagram about one example of the art of the mother liquor separated from the crystallization product is shown.

[Drawing 6] The explanatory view which attached the heat treatment equipment and the stagnation tub to the reaction distilling column is shown.

## [Description of Notations]

1 Reaction Process

2 Separation Process

3 Crystallizing Process

4 Crystallization Product Separation Process

5 Distillation Process

6 Heating Process (Reaction Vessel)

7 Reduced Pressure Recovery Process (Reduced Pressure Evaporation Column)

8 Strong Acid Mold Ion-Exchange-Resin Down Stream Processing

31, 32, 33, 34 Distilling column

35 Strong Acid Mold Ion-Exchange-Resin Processor

36 37 Settler

55 Outer Case

56 Container Liner

57 Microcrystal Adduct Solution Tank

R strong acid mold ion exchange resin -- a column

---

[Translation done.]

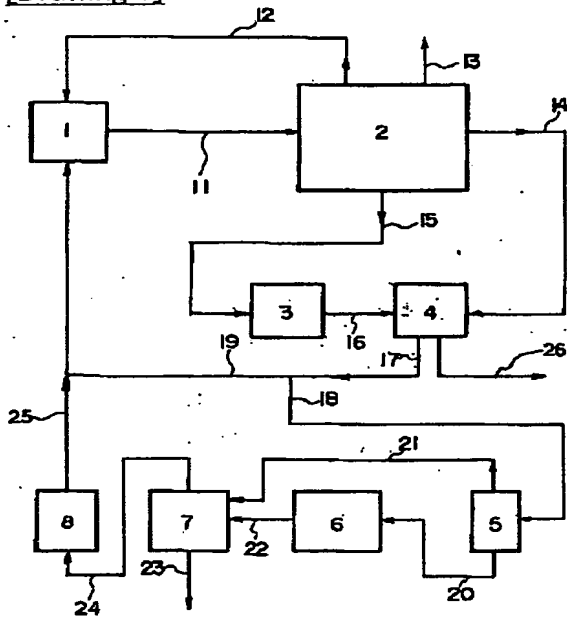
## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

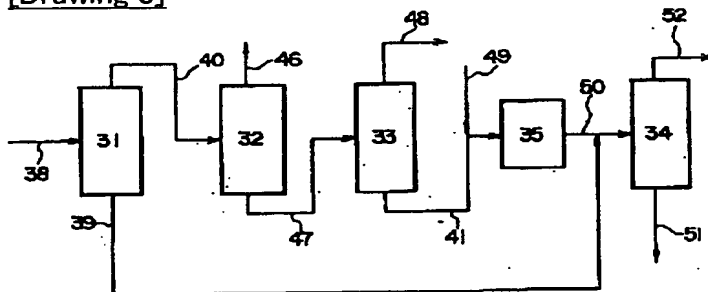
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

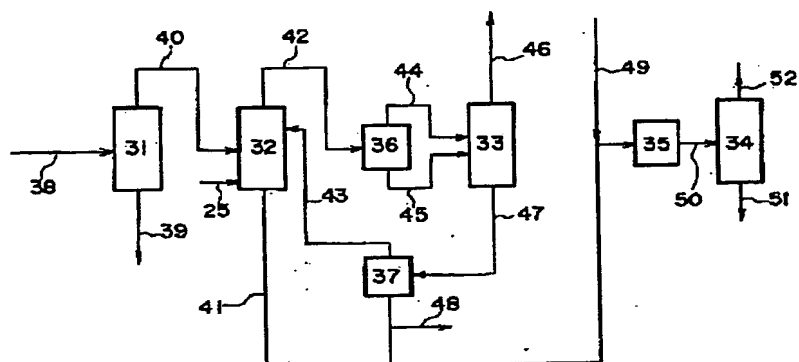
[Drawing 1]



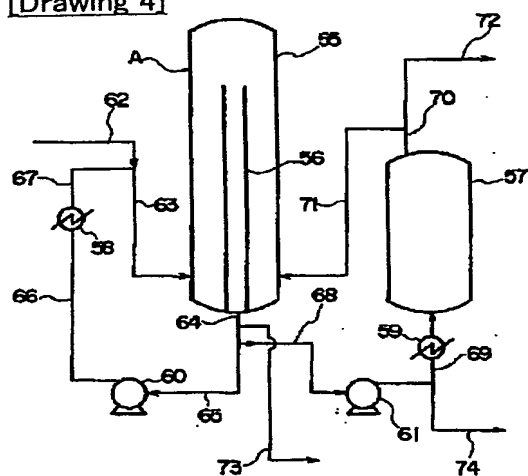
[Drawing 3]



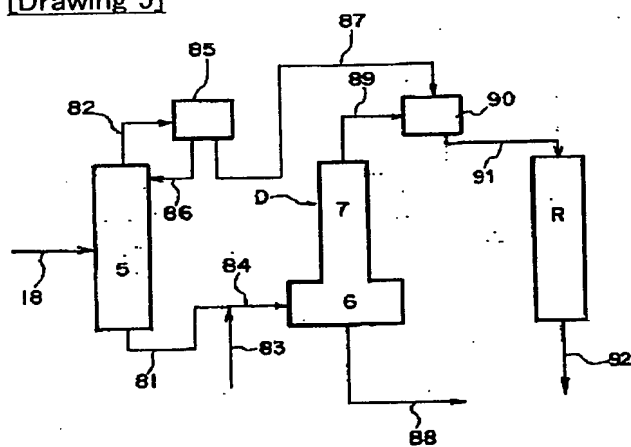
[Drawing 2]



[Drawing 4]

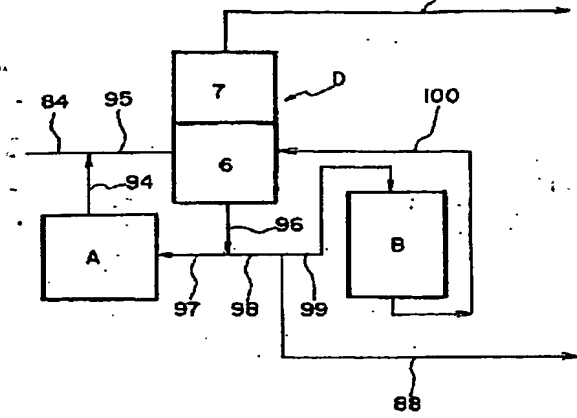


[Drawing 5]



[Drawing 6]





[Translation done.]

**THIS PAGE BLANK** (USPTO)